

Supporting Information

Exploiting Umpolung Reactivity of Diazo Group: Direct access to Triazolyl-Azaarenes from Azaarenes

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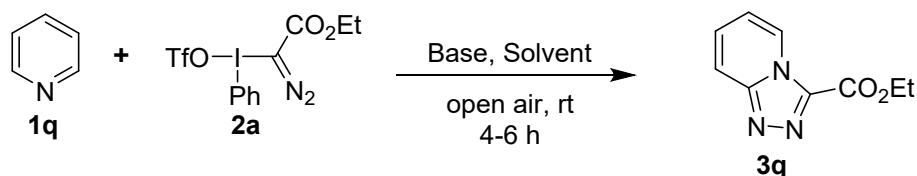
1. Experimental Section

1.1 General information

Until mentioned otherwise, all reactions were carried out under nitrogen atmosphere in flame-dried glassware. All reactions were monitored by Thin Layer Chromatography (TLC) and visualization was effected with UV and/or by developing in iodine. Melting points were recorded on a Precision melting point apparatus and are uncorrected. NMR spectra were recorded on a Bruker Avance spectrometer at 400/500 MHz (^1H), 100/125 MHz (^{13}C), 162 MHz (^{31}P) and 376 MHz (^{19}F). Chemical shifts are reported in δ (ppm) relative to TMS as the internal standard for ^1H and ^{13}C , TFA as the internal standard for ^{19}F and phosphoric acid as the external standard for ^{31}P . To describe spin multiplicity, standard abbreviations such as s, d, t, q, m, dd referring to singlet, doublet, triplet, quartet, multiplet and doublet of doublet respectively, are used. The ESI-HRMS spectra were recorded on Agilent 6520-Q-ToF LC/MS system.

All the chemicals, catalysts and solvents were purchased from commercial sources and used as received. The starting azaarenes **1b**, **1g**, **1j-1m**, **1o**, **1p**, **1u** were synthesized according to the standard protocols in literature.¹ All other azaarenes used in reactions were commercially available. The hypervalent iodine diazo reagents **2** were prepared following the reported procedure.²

1.2 Table S1. Optimization of reaction conditions for pyridine substrates^a



Entry	1q:2a	Solvent	Base (equiv)	Yield (%) ^b
1	1:1.2	CHCl_3	Na_2CO_3 (2)	37
2	1:2	CHCl_3	Na_2CO_3 (2)	47
3	2:1	CHCl_3	Na_2CO_3 (2)	68
4	2:1	DCM	Na_2CO_3 (2)	57

^aUnless otherwise noted, all reactions were carried out at 0.2 mmol scale of **1q** with specified amounts of **2a** and base in 2 mL solvent for 4-6 h in open air at rt; ^bisolated yields.

1.3 General procedure for the conversion of azaarenes **1** into 1,2,4-triazolyl-azaarenes **3**

In an oven dried 10 mL round bottom flask equipped with a magnetic stirring bar, the azaarene **1** (0.1 mmol or 0.2 mmol of pyridines), hypervalent iodine diazo reagent **2** (0.12 mmol or 0.1 mmol for pyridines) and Na_2CO_3 (0.2 mmol) were dissolved in chloroform (2

mL). The resulting reaction mixture was stirred at room temperature in open air atmosphere. After reaction completion (4-8 h; TLC monitoring), the reaction mixture was diluted with water (5 mL) and extracted with dichloromethane (5 mL x 3). The organic layer was washed with brine (5 mL x 3), dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on neutral silica gel (100-200 mesh) using hexane/ethyl acetate as eluent to afford the pure product **3**.

1.4 Procedure for the synthesis of [1,2,4]triazolo[3,4-*a*]isoquinoline **4³**

To a solution of ethyl [1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxylate **3a** (36 mg, 0.15 mmol) in THF (4 mL) was added a solution of LiOH.H₂O (13 mg, 0.45 mmol) in H₂O (2 mL). The mixture was stirred for 20 min, acidified with 2N aqueous HCl (pH 6) and extracted with DCM (5 mL x 3). The organic layer was washed with brine (5 mL x 3), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on neutral silica gel (100-200 mesh) using ethyl acetate/hexane (4:1) as eluent to afford the pure [1,2,4]triazolo[3,4-*a*]isoquinoline **4**.

1.5 Procedure for the synthesis of [1,2,4]triazolo[3,4-*a*]isoquinolin-3-ylmethanol **5⁴**

To a solution of ethyl [1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxylate **3a** (36 mg, 0.15 mmol) in anhydrous THF (5 mL) was added DIBAL-H (0.4 mL, 0.4 mmol, 1.0M) dropwise at 0 °C. The reaction mixture was stirred at 0 °C for another 1.5 h. Upon completion of reaction (TLC monitoring), the reaction was quenched with water (0.5 mL), 15% NaOH aqueous solution (0.2 mL) and DCM (5 mL). The resulting reaction mixture was warmed to room temperature, MgSO₄ was added and stirred for 15 min and filtered. The filter cake was washed with a mixed solvent of DCM/MeOH (10/1 (v/v), 10mL x 4). The filtrate was concentrated *in vacuo* and residue was purified by column chromatography on neutral silica gel (100-200 mesh) using MeOH/DCM (1:20) as eluent to afford the pure [1,2,4]triazolo[3,4-*a*]isoquinolin-3-ylmethanol **5**.

1.6 Procedure for the synthesis of *N*-benzyl-[1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxamide **6⁵**

In an oven dried 10 mL round bottom flask equipped with magnetic stirring bar, the ethyl [1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxylate **3a** (36 mg, 0.15 mmol) and benzylamine (18 mg, 0.17 mmol) were dissolved in EtOH (5 mL). The reaction mixture was refluxed for 2 h. Upon completion of reaction (TLC monitoring), EtOH was evaporated and residue was purified by column chromatography on neutral silica gel (100-200 mesh) using ethyl acetate/hexane (1:4) as eluent to afford the pure *N*-benzyl-[1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxamide **6**.

2. Details of X-ray Analysis of 3e

A good quality colorless single crystal of size 0.18 x 0.14 x 0.09 mm, was selected under a polarizing microscope and was mounted on a glass fiber for data collection. Single crystal X-ray data for compound **3e** was collected on the Rigaku Kappa 3 circle diffractometer equipped with the AFC12 goniometer and enhanced sensitivity (HG) Saturn724+ CCD detector in the 4x4 bin mode using the monochromated Mo-K α radiation generated from the microfocus sealed tube MicroMax-003 X-ray generator equipped with specially designed confocal multilayer optics. Data collection was performed using ω -scans of 0.5 $^\circ$ steps at 293(2) K. Cell determination, data collection and data reduction was performed using the Rigaku CrystalClear-SM Expert 2.1 b24 software.⁶ Structure solution and refinement were performed by using SHELXTL-NT.⁷ Refinement of coordinates and anisotropic thermal parameters of non-hydrogen atoms were carried out by the full-matrix least-squares method. The hydrogen atoms attached to carbon atoms were generated with idealized geometries and isotropically refined using a riding model.

Crystallization: Crystals of compound **3e** were grown from the solvent Chloroform: Methanol (1:3) by slow evaporation method (Figure S1; Table S2).

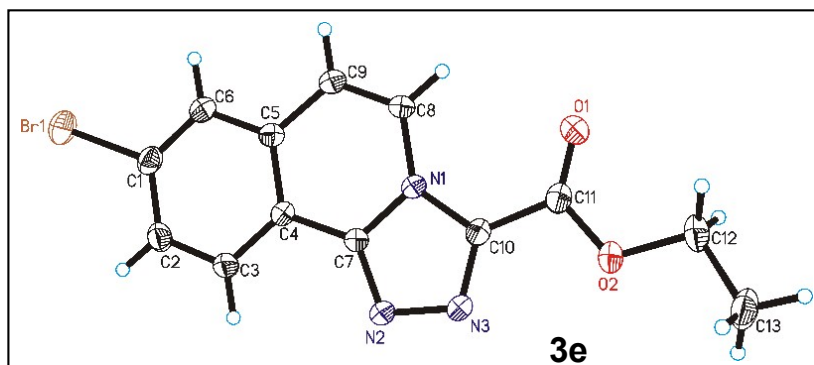


Figure S1. ORTEP diagram drawn with 30% ellipsoid probability for non-H atoms of the crystal structure of compound **3e** determined at 293 K.

Table S2. Crystal data and structure refinement details for **3e**

Compound	3e
Empirical formula	C ₁₃ H ₁₀ Br N ₃ O ₂
Formula weight	320.15
Crystal System	Triclinic
Space group	P-1
<i>a</i> (Å)	7.692(6)
<i>b</i> (Å)	7.901(2)
<i>c</i> (Å)	11.323(6)
α (°)	72.27(5)
β (°)	88.36(9)

γ (°)	75.68(6)
V (Å ³)	634.3(6)
Z	2
D_c (g/cm ³)	1.676
F_{000}	320
μ (mm ⁻¹)	4.447
θ_{\max} (°)	68.77
Total reflections	12288
Unique reflections	2281
Reflections [$I > 2\sigma(I)$]	1672
Parameters	173
R_{int}	0.1058
Goodness-of-fit	1.124
R [$F^2 > 2\sigma(F^2)$]	0.0545
wR (F^2 , all data)	0.1799
CCDC No.	2150459

3. Mass Spectra of 3ze-3zf (HRMS) and 3zh'-3zj' (ESMS)

Sample Name	HRMS22I28JAN22	Position	Vial 22	Instrument Name	Instrument 1	User Name	
Inj Vol	1	InjPosition		SampleType	Sample	IRM Calibration Status	Some Ions Missed
Data Filename	NRLD-667.d	ACQ Method	ISOCRATIC.m	Comment		Acquired Time	1/28/2022 12:42:32 PM

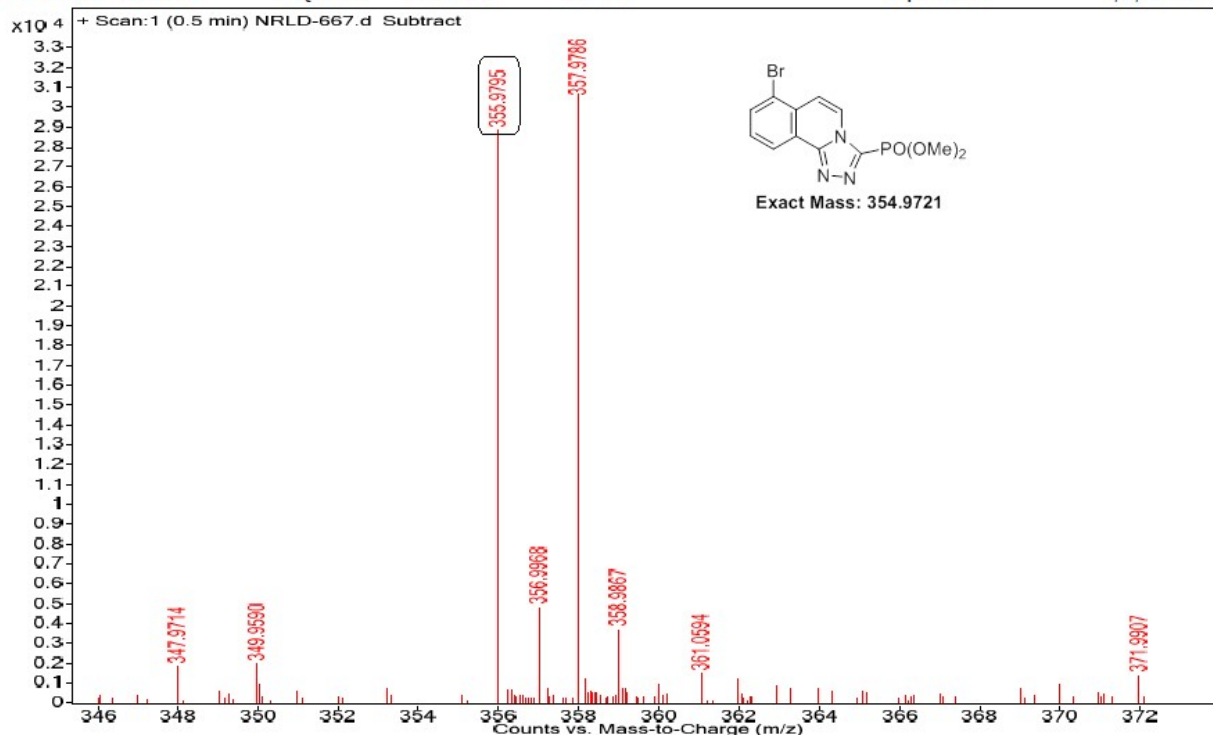


Figure S2. HRMS of 3ze

Sample Name	HRMS221033JAN16	Position	Vial 16	Instrument Name	Instrument 1	User Name	IRM Calibration Status	Some Ions Missed
Inj Vol	1	InjPosition		SampleType	Sample			
Data Filename	NRLD-682.d	ACQ Method	ISOCRATIC.m	Comment		Acquired Time		1/3/2022 12:34:50 PM

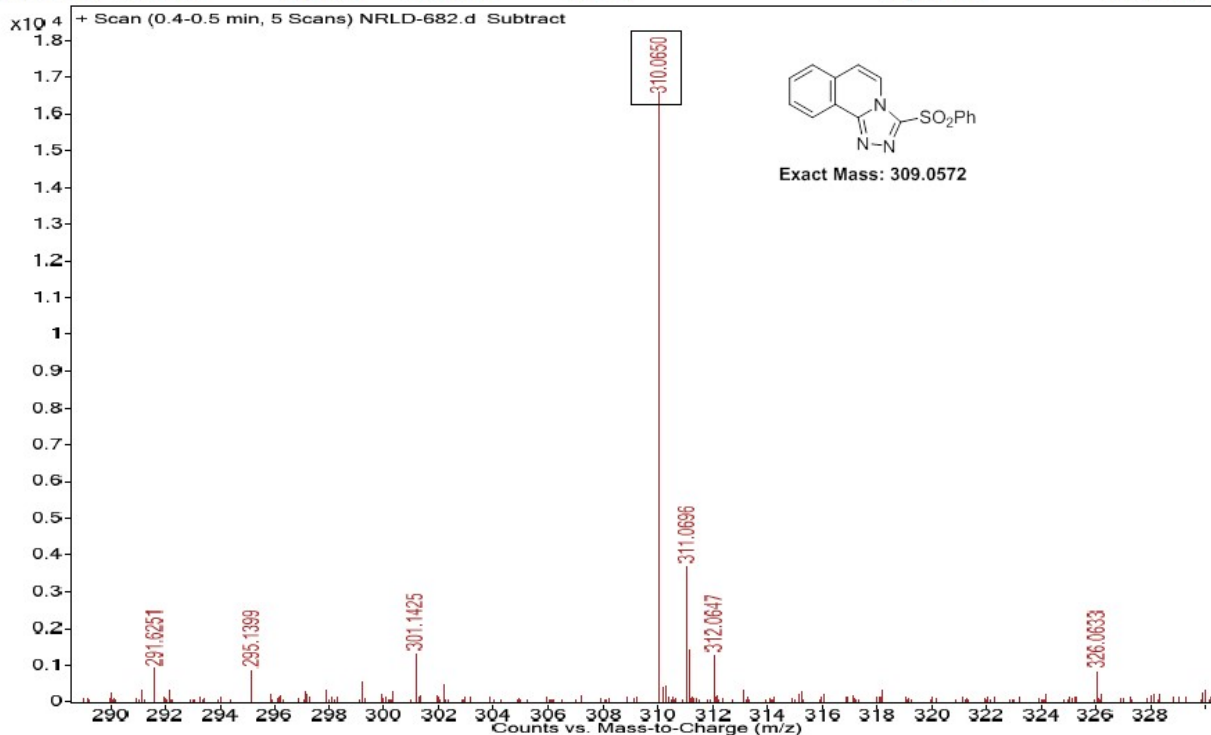


Figure S3. HRMS of 3zf

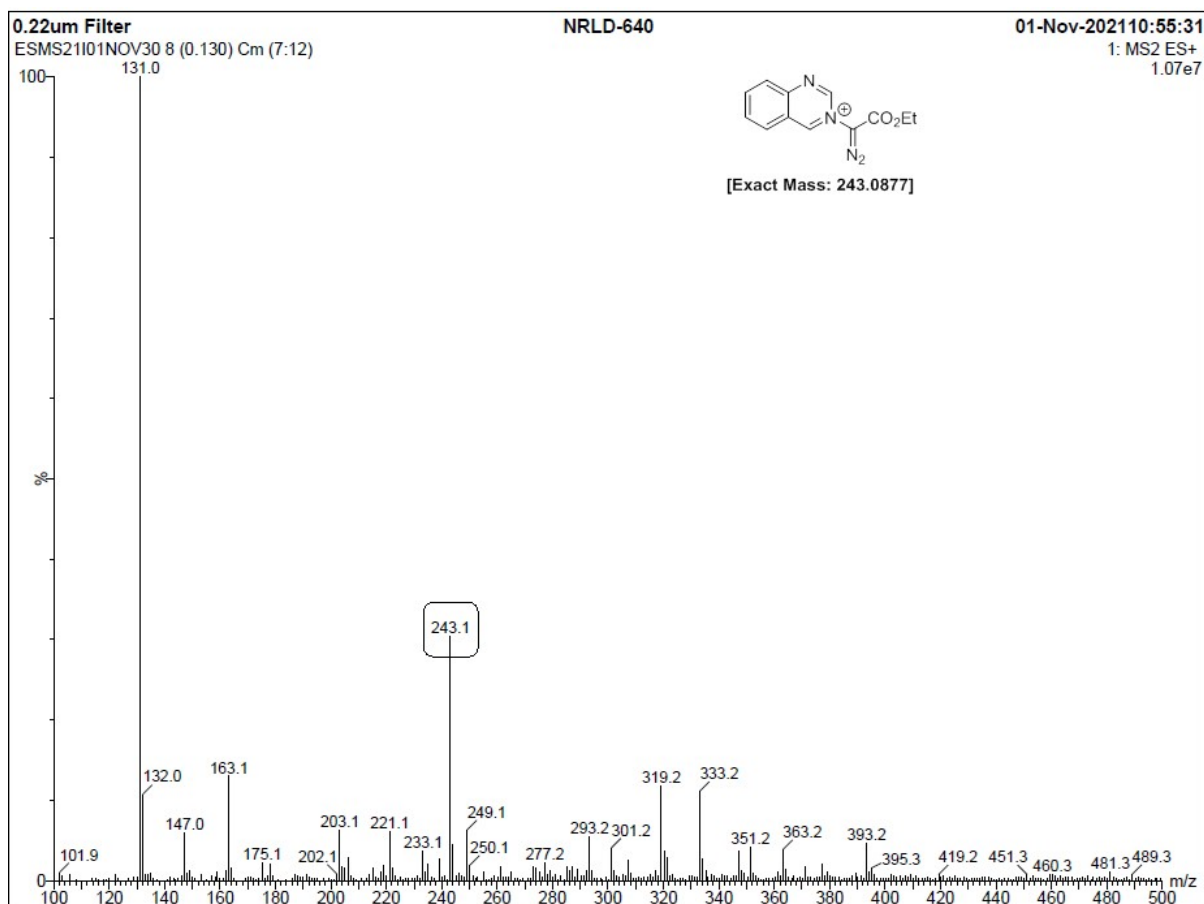


Figure S4. ESMS of 3zh'

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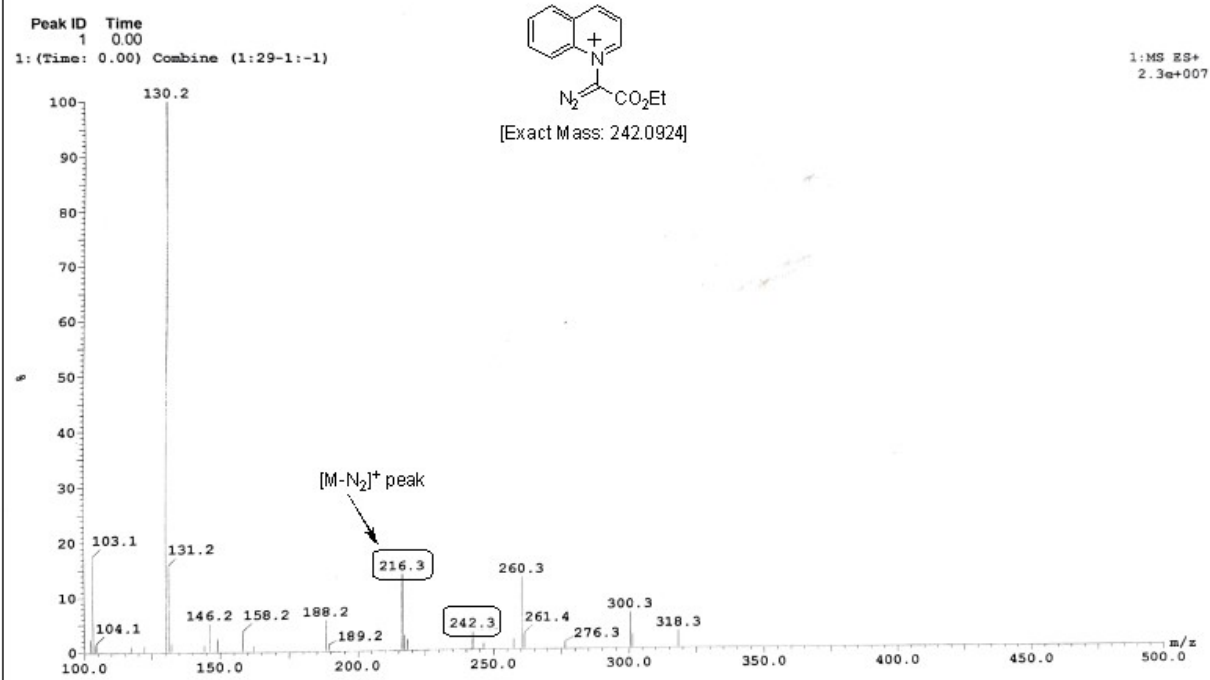


Figure S5. ESMS of 3zi'

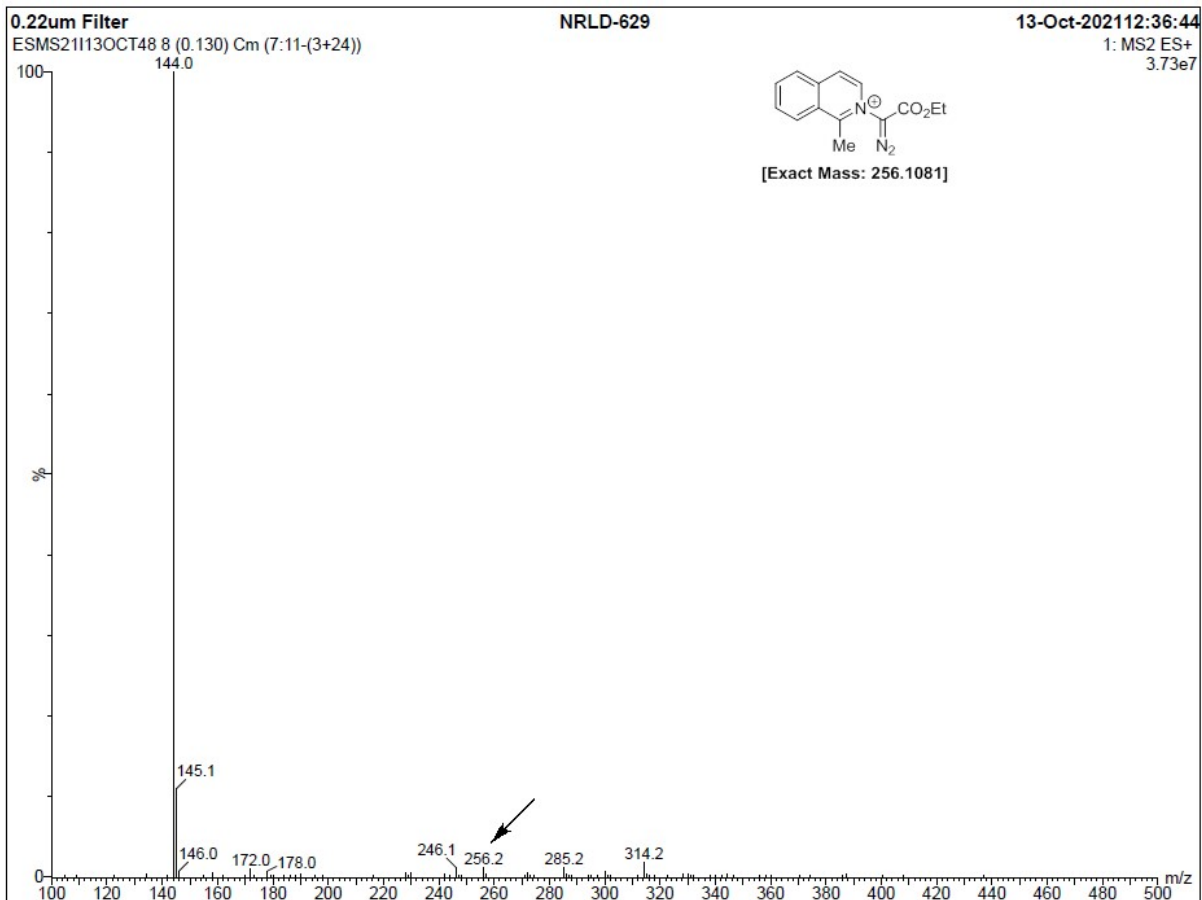
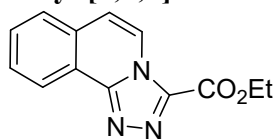


Figure S6. ESMS of 3zj'

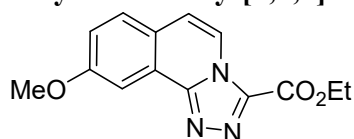
4. Spectroscopic Data

Ethyl [1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxylate (3a)



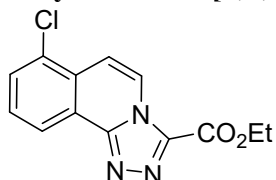
White solid; yield 71% (17 mg); R_f 0.50 (50% EtOAc/hexane); Mp 168-169 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.84-8.87 (m, 2H), 7.74-7.83 (m, 3H), 7.28 (d merged with solvent peak, $J = 7.4$ Hz, 1H), 4.60 (q, $J = 7.1$ Hz, 2H), 1.53 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 158.48, 150.24, 139.44, 130.97, 130.19, 129.44, 127.13, 124.60, 121.69, 120.91, 116.92, 62.50, 14.31; **HRMS** for $\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}_2$: calcd. $(\text{M}+\text{H})^+$: 242.0924, found: 242.0931

Ethyl 9-methoxy-[1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxylate (3b)



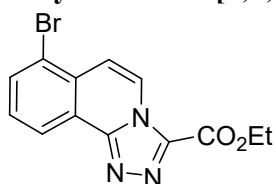
White solid; yield 70% (19 mg); R_f 0.50 (60% EtOAc/hexane); Mp 173-174 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.78 (d, $J = 7.3$ Hz, 1H), 8.22 (d, $J = 2.4$ Hz, 1H), 7.72 (d, $J = 8.8$ Hz, 1H), 7.34 (dd, $J = 8.8$ Hz, 2.6 Hz, 1H), 7.24 (d, $J = 7.3$ Hz, 1H), 4.60 (q, $J = 7.1$ Hz, 2H), 4.02 (s, 3H), 1.53 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 160.41, 158.49, 150.15, 139.41, 128.71, 124.33, 122.33, 121.79, 119.46, 116.63, 104.67, 62.44, 56.00, 14.32; **HRMS** for $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_3$: calcd. $(\text{M}+\text{H})^+$: 272.1030, found: 272.1027

Ethyl 7-chloro-[1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxylate (3c)



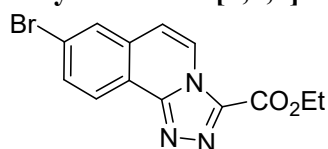
White solid; yield 65% (18 mg); R_f 0.50 (50% EtOAc/hexane); Mp 164-165 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.96 (d, $J = 7.7$ Hz, 1H), 8.80 (d, $J = 8.0$ Hz, 1H), 7.82 (d, $J = 7.8$ Hz, 1H), 7.74 (d, $J = 7.6$ Hz, 1H), 7.69 (t, $J = 7.9$ Hz, 1H), 4.61 (q, $J = 7.1$ Hz, 2H), 1.54 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 158.32, 149.71, 139.57, 131.92, 131.26, 129.82, 128.10, 123.38, 122.67, 122.43, 113.10, 62.68, 14.29; **HRMS** for $\text{C}_{13}\text{H}_{10}\text{ClN}_3\text{O}_2$: calcd. $(\text{M}+\text{H})^+$: 276.0534, found: 276.0535

Ethyl 7-bromo-[1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxylate (3d)



White solid; yield 60% (19 mg); R_f 0.50 (50% EtOAc/hexane); Mp 185-186 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.95 (d, $J = 7.7$ Hz, 1H), 8.85 (d, $J = 8.0$ Hz, 1H), 8.01 (dd, $J = 7.8$ Hz, 1.0 Hz, 1H), 7.72 (d, $J = 7.7$ Hz, 1H), 7.61 (t, $J = 7.9$ Hz, 1H), 4.62 (q, $J = 7.2$ Hz, 2H), 1.54 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 158.31, 149.69, 139.51, 134.83, 130.12, 129.51, 124.08, 122.78, 122.46, 122.10, 115.70, 62.68, 14.29; ; **HRMS** for $\text{C}_{13}\text{H}_{10}\text{BrN}_3\text{O}_2$: calcd. (M+H) $^+$: 320.0029, found: 320.0037

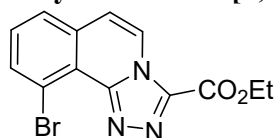
Ethyl 8-bromo-[1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxylate (3e)



White solid; yield 63% (20 mg); R_f 0.50 (50% EtOAc/hexane); Mp 206-207 °C; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.91 (d, $J = 7.5$ Hz, 1H), 8.72 (d, $J = 8.5$ Hz, 1H), 7.99 (s, 1H), 7.87 (d, $J = 8.6$ Hz, 1H), 7.21 (t, $J = 7.4$ Hz, 1H), 4.60 (q, $J = 7.1$ Hz, 2H), 1.52 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 158.37, 149.82, 139.58, 132.78, 131.54, 129.65, 126.19, 125.54, 122.91, 119.62, 115.73, 62.63, 14.28; **HRMS** for $\text{C}_{13}\text{H}_{10}\text{BrN}_3\text{O}_2$: calcd. (M+H) $^+$: 320.0029, found: 320.0036

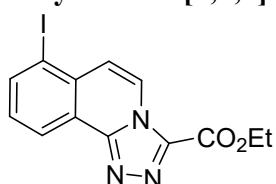
Selected X-Ray Crystallographic data for 3e: $\text{C}_{13}\text{H}_{10}\text{BrN}_3\text{O}_2$, $M = 320.15$, Triclinic, $P - 1$, $a = 7.692(6)$ Å, $b = 7.901(2)$ Å, $c = 11.323(6)$ Å, $V = 634.3(6)$ Å 3 , $\alpha = 72.27(5)$ °, $\beta = 88.36(9)$ °, $\gamma = 75.68(6)$ °, $Z = 2$, $D_c = 1.676$ g/cm 3 , μ (Mo-K α) = 4.447 mm $^{-1}$, $F(000) = 320$, Reflections collected: Unique 12288/2281 [$R_{\text{int}} = 0.1058$]. Final R indices [$I > 2\sigma(I)$], $R1 = 0.0545$, $wR2 = 0.1799$

Ethyl 10-bromo-[1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxylate (3f)



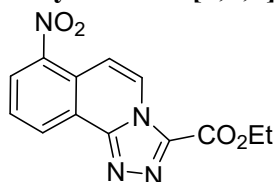
White solid; yield 47% (15 mg); R_f 0.50 (50% EtOAc/hexane); Mp 230-231 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.96 (d, $J = 7.4$ Hz, 1H), 8.06 (d, $J = 7.8$ Hz, 1H), 7.77 (d, $J = 7.9$ Hz, 1H), 7.55 (t, $J = 7.8$ Hz, 1H), 7.27 (d, $J = 7.3$ Hz, 1H), 4.60 (q, $J = 7.1$ Hz, 2H), 1.53 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 158.57, 148.99, 139.18, 135.65, 132.64, 130.65, 126.61, 122.30, 120.87, 120.12, 117.04, 62.58, 14.24; **HRMS** for $\text{C}_{13}\text{H}_{10}\text{BrN}_3\text{O}_2$: calcd. (M+H) $^+$: 320.0029, found: 320.0031

Ethyl 7-iodo-[1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxylate (3g)



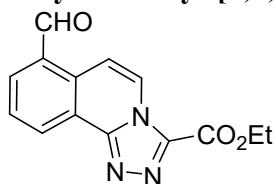
White solid; yield 52% (19 mg); R_f 0.50 (50% EtOAc/hexane); Mp 181-182 °C; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.91 (d, $J = 7.7$ Hz, 1H), 8.88 (d, $J = 8.1$ Hz, 1H), 8.29 (d, $J = 7.7$ Hz, 1H), 7.60 (d, $J = 7.7$ Hz, 1H), 7.45 (t, $J = 7.8$ Hz, 1H), 4.61 (q, $J = 7.1$ Hz, 2H), 1.54 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 158.30, 149.74, 141.95, 139.39, 132.18, 130.45, 124.99, 122.91, 121.86, 120.59, 97.58, 62.66, 14.29; **HRMS** for $\text{C}_{13}\text{H}_{10}\text{IN}_3\text{O}_2$: calcd. (M+H) $^+$: 367.9890, found: 367.9887

Ethyl 7-nitro-[1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxylate (3h)



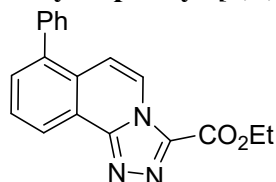
White solid; yield 56% (16 mg); R_f 0.50 (60% EtOAc/hexane); Mp 181-182 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.23 (d, $J = 8.0$ Hz, 1H), 9.07 (d, $J = 7.9$ Hz, 1H), 8.50 (d, $J = 7.8$ Hz, 1H), 8.14 (d, $J = 7.9$ Hz, 1H), 7.91 (t, $J = 8.0$ Hz, 1H), 4.63 (q, $J = 7.1$ Hz, 2H), 1.55 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 158.11, 148.91, 145.83, 139.84, 130.37, 128.90, 127.71, 124.80, 123.34, 122.71, 111.23, 62.93, 14.26; **HRMS** for $\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_4$: calcd. (M+H) $^+$: 287.0775, found: 287.0777

Ethyl 7-formyl-[1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxylate (3i)



White solid; yield 60% (16 mg); R_f 0.50 (60% EtOAc/hexane); Mp 171-172 °C; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 10.38 (s, 1H), 9.18 (d, $J = 8.0$ Hz, 1H), 9.03 (d, $J = 7.8$ Hz, 1H), 8.79 (d, $J = 7.8$ Hz, 1H), 8.24 (dd, $J = 7.4$ Hz, 1.1 Hz, 1H), 7.95-7.98 (m, 1H), 4.62 (q, $J = 7.2$ Hz, 2H), 1.54 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 192.59, 158.27, 149.47, 139.61, 138.70, 130.88, 130.43, 128.97, 128.57, 124.30, 122.14, 112.85, 62.71, 14.28; **HRMS** for $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_3$: calcd. (M+H) $^+$: 270.0873, found: 270.0880

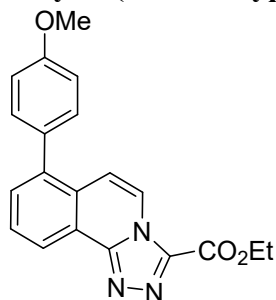
Ethyl 7-phenyl-[1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxylate (3j)



White solid; yield 47% (15 mg); R_f 0.50 (50% EtOAc/hexane); Mp 199-200 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.91 (d, $J = 7.9$ Hz, 1H), 8.79 (d, $J = 7.6$ Hz, 1H), 7.81 (d, $J = 7.8$ Hz, 1H), 7.72 (d, $J = 7.4$ Hz, 1H), 7.45-7.55 (m, 5H), 7.38 (d, $J = 7.6$ Hz, 1H), 4.59 (q, $J = 7.1$ Hz, 2H), 1.52 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 158.45, 150.51, 140.40,

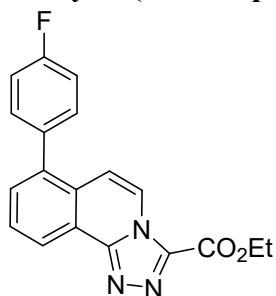
139.43, 139.05, 131.97, 129.85, 129.00, 128.71, 128.20, 128.08, 123.89, 121.46, 121.41, 114.92, 62.49, 14.31; **HRMS** for C₁₉H₁₅N₃O₂: calcd. (M+H)⁺: 318.1237, found: 318.1245

Ethyl 7-(4-methoxyphenyl)-[1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxylate (3k)



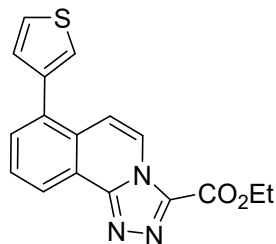
White solid; yield 63% (22 mg); *R_f* 0.50 (60% EtOAc/hexane); Mp 210-211 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.88 (d, *J* = 7.9 Hz, 1H), 8.79 (d, *J* = 7.7 Hz, 1H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 6.7 Hz, 1H), 7.37-7.41 (m, 3H), 7.06 (d, *J* = 8.6 Hz, 2H), 4.59 (q, *J* = 7.1 Hz, 2H), 3.91 (s, 3H), 1.52 (t, *J* = 7.1 Hz, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 159.57, 158.47, 150.57, 140.14, 139.41, 131.98, 131.36, 130.99, 128.98, 128.35, 123.55, 121.44, 121.31, 115.02, 114.18, 62.45, 55.43, 14.30; ; **HRMS** for C₂₀H₁₇N₃O₃: calcd. (M+H)⁺: 348.1343, found: 348.1343

Benzyl 7-(4-fluorophenyl)-[1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxylate (3l)



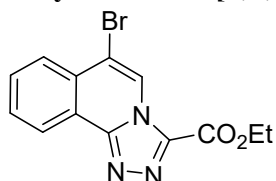
White solid; yield 45% (15 mg); *R_f* 0.50 (50% EtOAc/hexane); Mp 242-243 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.94 (d, *J* = 8.0 Hz, 1H), 8.83 (d, *J* = 7.7 Hz, 1H), 7.82 (t, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 7.4 Hz, 1H), 7.43-7.47 (m, 2H), 7.34 (d, *J* = 7.7 Hz, 2H), 7.23-7.28 (m merged with solvent peak, 2H), 4.61 (q, *J* = 7.1 Hz, 2H), 1.55 (t, *J* = 7.1 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 162.69 (d, *J*_{C-F} = 246.4 Hz), 158.42, 150.41, 139.44, 139.28, 135.00 (d, *J*_{C-F} = 3.4 Hz), 132.00, 131.49 (d, *J*_{C-F} = 8.0 Hz), 129.01, 128.22, 124.06, 121.64, 121.44, 115.75 (d, *J*_{C-F} = 21.4 Hz), 114.60, 62.52, 14.29; **¹⁹F NMR** (376 MHz, CDCl₃) δ -113.79 (s); **HRMS** for C₁₉H₁₄FN₃O₂: calcd. (M+H)⁺: 336.1143, found: 336.1144

Ethyl 7-(thiophen-3-yl)-[1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxylate (3m)



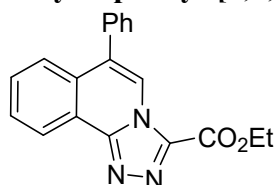
White solid; yield 46% (15 mg); R_f 0.50 (50% EtOAc/hexane); Mp 149-150 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.88 (dd, $J = 6.6$ Hz, $J = 2.7$ Hz, 1H), 8.82 (d, $J = 7.7$ Hz, 1H), 7.75-7.80 (m, 2H), 7.50-7.54 (m, 2H), 7.42-7.43 (m, 1H), 7.26-7.28 (m, 1H merged with solvent peak), 4.60 (q, $J = 7.1$ Hz, 2H), 1.53 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 158.43, 150.44, 139.43, 135.14, 131.91, 129.08, 129.04, 128.40, 126.42, 124.45, 123.92, 121.54, 121.45, 114.80, 62.50, 14.30; **HRMS** for $\text{C}_{17}\text{H}_{13}\text{N}_3\text{O}_2\text{S}$: calcd. $(\text{M}+\text{H})^+$: 324.0801, found: 324.0803

Ethyl 6-bromo-[1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxylate (3n)



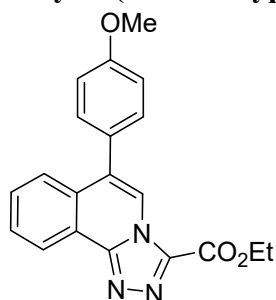
Yellow solid; yield 44% (14 mg); R_f 0.50 (50% EtOAc/hexane); Mp 171-172 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.24 (s, 1H), 8.90 (d, $J = 7.6$ Hz, 1H), 8.19 (d, $J = 8.2$ Hz, 1H), 7.82-7.90 (m, 2H), 4.61 (q, $J = 7.1$ Hz, 2H), 1.54 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 158.29, 149.57, 138.91, 131.77, 130.42, 129.11, 127.22, 124.88, 122.54, 120.64, 113.57, 62.78, 14.27; **HRMS** for $\text{C}_{13}\text{H}_{10}\text{BrN}_3\text{O}_2$: calcd. $(\text{M}+\text{H})^+$: 320.0029, found: 320.0030

Ethyl 6-phenyl-[1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxylate (3o)



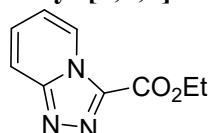
White solid; yield 69% (22 mg); R_f 0.50 (40% EtOAc/hexane); Mp 210-211 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.97 (d, $J = 7.7$ Hz, 1H), 8.86 (s, 1H), 7.69-7.80 (m, 3H), 7.50-7.55 (m, 5H), 4.59 (q, $J = 7.1$ Hz, 2H), 1.52 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 158.52, 149.92, 139.51, 135.22, 130.86, 130.40, 130.38, 130.07, 129.30, 128.83, 128.75, 126.22, 124.86, 120.93, 120.36, 62.49, 14.30; **HRMS** for $\text{C}_{19}\text{H}_{15}\text{N}_3\text{O}_2$: calcd. $(\text{M}+\text{H})^+$: 318.1237, found: 318.1240

Ethyl 6-(4-methoxyphenyl)-[1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxylate (3p)



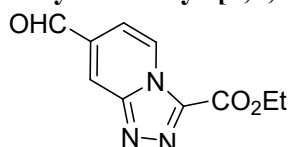
White solid; yield 46% (16 mg); R_f 0.50 (60% EtOAc/hexane); Mp 142-143 °C; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.95 (d, $J = 7.6$ Hz, 1H), 8.83 (s, 1H), 7.76-7.79 (m, 1H), 7.70-7.73 (m, 1H), 7.43 (d, $J = 8.3$ Hz, 2H), 7.07 (d, $J = 8.4$ Hz, 2H), 4.58 (q, $J = 7.1$ Hz, 2H), 3.91 (s, 3H), 1.52 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 160.04, 158.54, 149.91, 139.46, 131.23, 130.80, 130.67, 130.10, 129.22, 127.39, 126.25, 124.85, 120.93, 120.20, 114.29, 62.45, 55.45, 14.29; **HRMS** for $\text{C}_{20}\text{H}_{17}\text{N}_3\text{O}_3$: calcd. (M+H) $^+$: 348.1343, found: 348.1344

Ethyl [1,2,4]triazolo[4,3-*a*]pyridine-3-carboxylate (3q)



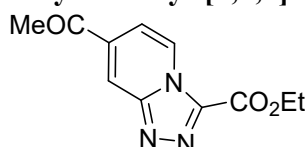
White solid; yield 68% (13 mg); R_f 0.50 (80% EtOAc/hexane); Mp 152-153 °C; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.18 (d, $J = 6.9$ Hz, 1H), 7.97 (d, $J = 9.2$ Hz, 1H), 7.48-7.51 (m, 1H), 7.12 (t, $J = 6.8$ Hz, 1H), 4.59 (q, $J = 7.1$ Hz, 2H), 1.52 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 158.45, 151.45, 137.81, 129.19, 125.92, 116.60, 116.00, 62.38, 14.30; **HRMS** for $\text{C}_9\text{H}_9\text{N}_3\text{O}_2$: calcd. (M+H) $^+$: 192.0768, found: 192.0763

Ethyl 7-formyl-[1,2,4]triazolo[4,3-*a*]pyridine-3-carboxylate (3r)



White solid; yield 46% (10 mg); R_f 0.50 (60% EtOAc/hexane); Mp 153-154 °C; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 10.12 (s, 1H), 9.25 (d, $J = 7.2$ Hz, 1H), 8.44 (s, 1H), 7.59 (d, $J = 7.2$ Hz, 1H), 4.62 (q, $J = 7.2$ Hz, 2H), 1.53 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 188.86, 158.11, 151.06, 138.81, 136.06, 126.78, 122.23, 111.95, 62.90, 14.25; **HRMS** for $\text{C}_{10}\text{H}_9\text{N}_3\text{O}_3$: calcd. (M+H) $^+$: 220.0717, found: 220.0715

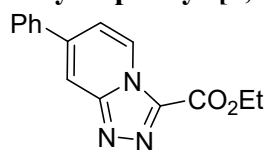
Ethyl 7-acetyl-[1,2,4]triazolo[4,3-*a*]pyridine-3-carboxylate (3s)



White solid; yield 55% (12 mg); R_f 0.50 (70% EtOAc/hexane); Mp 219-220 °C; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.18 (d, $J = 7.3$ Hz, 1H), 8.49 (s, 1H), 7.67 (dd, $J = 7.3$ Hz, 1.4 Hz, 1H),

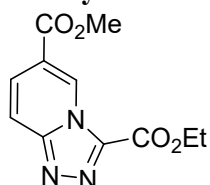
4.60 (q, $J = 7.2$ Hz, 2H), 2.73 (s, 3H), 1.53 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 194.81, 158.16, 151.18, 138.54, 136.74, 126.01, 118.00, 113.59, 62.77, 26.19, 14.26; HRMS for $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}_3$: calcd. $(\text{M}+\text{H})^+$: 234.0873, found: 234.0864

Ethyl 7-phenyl-[1,2,4]triazolo[4,3-*a*]pyridine-3-carboxylate (3t)



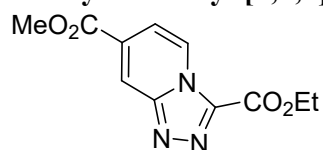
White solid; yield 37% (10 mg); R_f 0.50 (60% EtOAc/hexane); Mp 199-200 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.19 (dd, $J = 7.3$ Hz, 1.0 Hz, 1H), 8.11-8.11 (m, 1H), 7.69-7.71 (m, 2H), 7.47-7.56 (m, 3H), 7.40 (dd, $J = 7.3$ Hz, 1.2 Hz, 1H) 4.60 (q, $J = 7.1$ Hz, 2H), 1.53 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.45, 152.21, 142.39, 137.57, 137.08, 129.57, 129.42, 127.10, 125.71, 116.25, 112.63, 62.39, 14.32; HRMS for $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_2$: calcd. $(\text{M}+\text{H})^+$: 268.1081, found: 268.1074

3-Ethyl 6-methyl [1,2,4]triazolo[4,3-*a*]pyridine-3,6-dicarboxylate (3u)



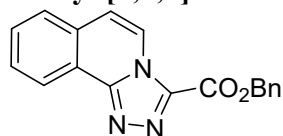
White solid; yield 52% (13 mg); R_f 0.50 (60% EtOAc/hexane); Mp 147-148 °C; ^1H NMR (500 MHz, CDCl_3) δ 9.85 (s, 1H), 8.03 (dd, $J = 9.5$ Hz, 1.5 Hz, 1H), 7.96 (dd, $J = 9.5$ Hz, 0.9 Hz, 1H), 4.61 (q, $J = 7.1$ Hz, 2H), 4.01 (s, 3H), 1.53 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.06, 158.12, 151.42, 138.65, 129.82, 128.88, 120.27, 116.08, 62.76, 52.97, 14.24; HRMS for $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}_4$: calcd. $(\text{M}+\text{H})^+$: 250.0822, found: 250.0825

3-Ethyl 7-methyl [1,2,4]triazolo[4,3-*a*]pyridine-3,7-dicarboxylate (3v)



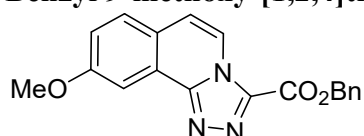
White solid; yield 48% (12 mg); R_f 0.50 (60% EtOAc/hexane); Mp 128-129 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.20 (dd, $J = 7.2$ Hz, 0.8 Hz, 1H), 8.64 (s, 1H), 7.68 (dd, $J = 7.2$ Hz, 1.3 Hz, 1H), 4.61 (q, $J = 7.1$ Hz, 2H), 4.03 (s, 3H) 1.53 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.18, 158.21, 151.05, 138.41, 130.91, 125.79, 119.03, 115.07, 62.70, 53.18, 14.26; HRMS for $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}_4$: calcd. $(\text{M}+\text{H})^+$: 250.0822, found: 250.0823

Benzyl [1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxylate (3w)



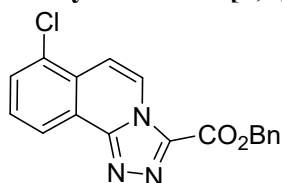
White solid; yield 69% (21 mg); R_f 0.50 (40% EtOAc/hexane); Mp 158-159 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.85 (d, $J = 7.4$ Hz, 2H), 7.79-7.82 (m, 1H), 7.73-7.77 (m, 2H), 7.54-7.56 (m, 2H), 7.34-7.42 (m, 3H), 7.28 (d, $J = 7.4$ Hz, 1H), 5.56 (s, 2H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 158.32, 150.31, 139.28, 134.94, 131.01, 130.22, 129.48, 128.73, 128.71, 127.13, 124.64, 121.68, 120.91, 116.97, 67.84; **HRMS** for $\text{C}_{18}\text{H}_{13}\text{N}_3\text{O}_2$: calcd. $(\text{M}+\text{H})^+$: 304.1081, found: 304.1089

Benzyl 9-methoxy-[1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxylate (3x)



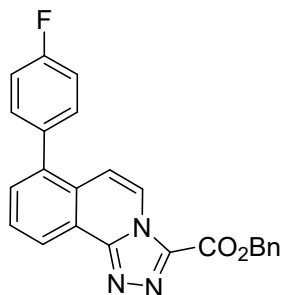
White solid; yield 66% (22 mg); R_f 0.50 (60% EtOAc/hexane); Mp 163-164 °C; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.76 (d, $J = 7.3$ Hz, 1H), 8.21 (d, $J = 2.4$ Hz, 1H), 7.71 (d, $J = 8.8$ Hz, 1H), 7.55 (d, $J = 7.1$ Hz, 2H), 7.34-7.42 (m, 4H), 7.23 (d, $J = 7.3$ Hz, 1H), 5.56 (s, 2H), 4.02 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 160.45, 159.03, 158.32, 150.21, 139.24, 134.97, 128.79, 128.73, 128.72, 124.37, 122.32, 121.87, 119.45, 116.72, 104.69, 67.82, 56.02; **HRMS** for $\text{C}_{19}\text{H}_{15}\text{N}_3\text{O}_3$: calcd. $(\text{M}+\text{H})^+$: 334.1186, found: 334.1196

Benzyl 7-chloro-[1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxylate (3y)



White solid; yield 50% (17 mg); R_f 0.50 (40% EtOAc/hexane); Mp 145-146 °C; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.94 (d, $J = 7.6$ Hz, 1H), 8.80 (d, $J = 7.9$ Hz, 1H), 7.82 (d, $J = 7.5$ Hz, 1H), 7.72 (d, $J = 7.6$ Hz, 1H), 7.68 (t, $J = 8.0$ Hz, 1H), 7.56 (d, $J = 7.0$ Hz, 2H), 7.35-7.42 (m, 3H), 5.57 (s, 2H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 158.17, 149.78, 139.44, 134.79, 131.94, 131.30, 129.85, 128.79, 128.77, 128.74, 128.13, 123.41, 122.66, 122.43, 113.15, 68.02; **HRMS** for $\text{C}_{18}\text{H}_{12}\text{ClN}_3\text{O}_2$: calcd. $(\text{M}+\text{H})^+$: 338.0691, found: 338.0693

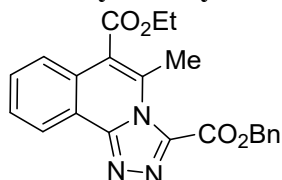
Benzyl 7-(4-fluorophenyl)-[1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxylate (3z)



White solid; yield 55% (22 mg); R_f 0.50 (50% EtOAc/hexane); Mp 225-226 °C; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.90 (d, $J = 8.0$ Hz, 1H), 8.78 (d, $J = 7.7$ Hz, 1H), 7.79 (t, $J = 7.8$ Hz, 1H), 7.68 (d, $J = 7.3$ Hz, 1H), 7.54 (d, $J = 7.2$ Hz, 2H), 7.34-7.43 (m, 5H), 7.30 (d, $J = 7.7$

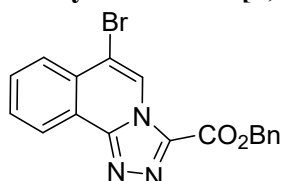
Hz, 1H), 7.23 (t, $J = 8.6$ Hz, 2H), 5.55 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 162.71 (d, $J_{\text{C-F}} = 246.1$ Hz), 158.24, 150.47, 139.29, 134.98 (d, $J_{\text{C-F}} = 3.5$ Hz), 134.88, 132.05, 131.49 (d, $J_{\text{C-F}} = 8.0$ Hz), 129.04, 128.74, 128.73, 128.23, 124.08, 121.63, 121.43, 115.77 (d, $J_{\text{C-F}} = 21.4$ Hz), 114.65, 67.87; ^{19}F NMR (376 MHz, CDCl_3) δ -113.76 (s); HRMS for $\text{C}_{24}\text{H}_{16}\text{FN}_3\text{O}_2$: calcd. (M+H) $^+$: 398.1299, found: 398.1294

3-Benzyl 6-ethyl 5-methyl-[1,2,4]triazolo[3,4-*a*]isoquinoline-3,6-dicarboxylate (3za)



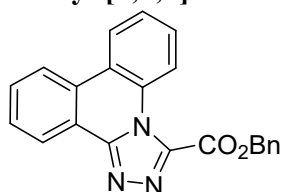
White solid; yield 59% (23 mg); R_f 0.50 (35% EtOAc/hexane); Mp 103-104 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.83-8.86 (m, 1H), 7.66-7.74 (m, 3H), 7.52 (br d, $J = 6.7$ Hz, 2H), 7.36-7.42 (m, 3H), 5.54 (s, 2H), 4.54 (q, $J = 7.1$ Hz, 2H), 2.62 (s, 3H), 1.46 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.63, 159.17, 149.76, 142.20, 134.58, 131.18, 130.51, 129.17, 128.83, 128.76, 128.69, 127.89, 124.74, 124.40, 121.62, 119.81, 68.71, 62.43, 18.40, 14.23; HRMS for $\text{C}_{22}\text{H}_{19}\text{N}_3\text{O}_4$: calcd. (M+H) $^+$: 390.1448, found: 390.1452

Benzyl 6-bromo -[1,2,4]triazolo[3,4-*a*]isoquinoline-3-carboxylate (3zb)



Yellow solid; yield 52% (20 mg); R_f 0.50 (40% EtOAc/hexane); Mp 202-203 $^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 9.19 (s, 1H), 8.87 (d, $J = 7.6$ Hz, 1H), 8.15 (d, $J = 7.9$ Hz, 1H), 7.80-7.87 (m, 2H), 7.55 (d, $J = 7.1$ Hz, 2H), 7.34-7.41 (m, 3H), 5.56 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.13, 149.58, 138.73, 134.77, 131.77, 130.42, 129.09, 128.81, 128.77, 128.74, 127.19, 124.87, 122.51, 120.59, 113.59, 68.11; HRMS for $\text{C}_{18}\text{H}_{12}\text{BrN}_3\text{O}_2$: calcd. (M+H) $^+$: 382.0186, found: 382.0181

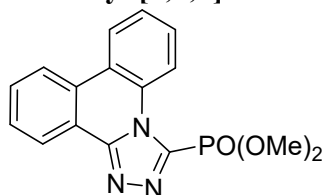
Benzyl [1,2,4]triazolo[4,3-*f*]phenanthridine-3-carboxylate (3zc)



White solid; 48% (17 mg); R_f 0.50 (50% EtOAc/hexane); Mp 190-191 $^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 8.82 (d, $J = 7.6$ Hz, 1H), 8.41 (d, $J = 7.8$ Hz, 1H), 8.34 (t, $J = 8.4$ Hz, 2H), 7.66-7.77 (m, 2H), 7.48-7.57 (m, 4H), 7.37-7.43 (m, 3H), 5.61 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.87, 150.04, 142.88, 134.72, 131.22, 129.97, 129.21, 129.04, 128.98, 128.80,

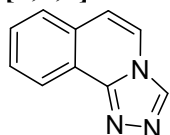
128.78, 127.25, 125.56, 124.13, 123.07, 122.41, 120.43, 119.49, 68.60; **HRMS** for $C_{22}H_{15}N_3O_2$: calcd. (M+H)⁺: 354.1237, found: 354.1242

Dimethyl [1,2,4]triazolo[4,3-f]phenanthridin-3-ylphosphonate (3zd)



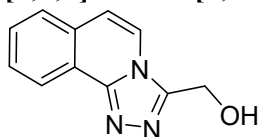
Colorless liquid; yield 34% (11 mg); R_f 0.50 (80% EtOAc/hexane); **¹H NMR** (500 MHz, $CDCl_3$) δ 9.02 (d, $J = 8.4$ Hz, 1H), 8.87 (d, $J = 7.7$ Hz, 1H), 8.51 (d, $J = 8.0$ Hz, 1H), 8.42 (d, $J = 8.2$ Hz, 1H), 7.81 (t, $J = 7.2$ Hz, 1H), 7.72-7.76 (m, 2H), 7.66 (t, $J = 7.6$ Hz, 1H), 4.07 (d, $^3J_{H-P} = 11.5$ Hz, 6H); **¹³C NMR** (100 MHz, $CDCl_3$) δ 150.62, 131.31, 130.30, 129.76, 129.22, 129.07, 127.29, 125.65, 124.11, 122.89, 122.49, 120.43, 119.75, 55.09 (d, $^2J_{C-P} = 6.7$ Hz); **³¹P NMR** (161.9 MHz, $DMSO-d_6$) δ 0.50; **HRMS** for $C_{16}H_{14}N_3O_3P$: calcd. (M+H)⁺: 328.0846, found: 328.0847

[1,2,4]triazolo[3,4-a]isoquinoline (4)



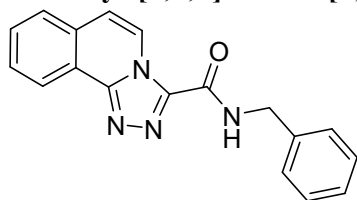
White solid; yield 75% (19 mg); R_f 0.50 (EtOAc); Mp 95-96 °C; **¹H NMR** (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.75 (d, $J = 7.1$ Hz, 1H), 7.90 (d, $J = 7.2$ Hz, 1H), 7.68-7.76 (m, 3H), 7.11 (d, $J = 7.2$ Hz, 1H); **¹³C NMR** (100 MHz, $CDCl_3$) δ 148.23, 137.10, 130.22, 130.02, 129.30, 127.26, 124.16, 121.44, 119.78, 115.64; **HRMS** for $C_{10}H_7N_3$: calcd. (M+H)⁺: 170.0713, found: 170.0707.

[1,2,4]triazolo[3,4-a]isoquinolin-3-ylmethanol (5)



White solid; yield 60% (18 mg); R_f 0.50 (5% MeOH/DCM); Mp 181-182 °C; **¹H NMR** (400 MHz, $DMSO-d_6$) δ 8.53 (d, $J = 4.3$ Hz, 1H), 8.28 (d, $J = 7.0$ Hz, 1H), 7.95 (d, $J = 4.2$ Hz, 1H), 7.75-7.77 (m, 2H), 7.35 (d, $J = 7.1$ Hz, 1H), 5.80 (t, $J = 5.5$ Hz, 1H), 5.00 (d, $J = 4.9$ Hz, 2H); **¹³C NMR** (100 MHz, $DMSO-d_6$) δ 149.03, 148.42, 130.60, 130.22, 129.41, 128.04, 123.41, 121.72, 121.13, 114.53, 54.15; **HRMS** for $C_{11}H_9N_3O$: calcd. (M+H)⁺: 200.0818, found: 200.0821.

N-benzyl-[1,2,4]triazolo[3,4-a]isoquinoline-3-carboxamide (6)



White solid; yield 52% (24 mg); R_f 0.50 (30% EtOAc/hexane); Mp 234-235 °C; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.06 (dd, $J = 7.4$ Hz, 1.0 Hz, 1H), 8.77 (t, $J = 4.6$ Hz, 1H), 7.95 (br s, 1H), 7.78-7.79 (m, 1H), 7.72-7.74 (m, 2H), 7.22-7.39 (m merged with solvent peak, 6H), 4.71 (d, $J = 6.0$ Hz, 2H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 157.71, 150.28, 137.34, 130.79, 130.19, 129.26, 128.85, 127.88, 127.80, 127.19, 124.37, 122.29, 120.98, 116.45, 43.35; **HRMS** for $\text{C}_{18}\text{H}_{14}\text{N}_4\text{O}$: calcd. $(\text{M}+\text{H})^+$: 303.1240, found: 303.1244.

5. References

1. (a) R. Kuczniery, J. Dickhaut, H. Leinert and W. von der Saal, *Synth. Commun.*, 1999, **29**, 1617-1625; (b) S. A. Gamage, J. A. Spicer, G. W. Rewcastle, J. Milton, S. Sohal, W. Dangerfield, P. Mistry, N. Vicker, P. A. Charlton and W. A. Denny. *J. Med. Chem.* 2002, **45**, 740-743; (c) N. Jha, R. P. Singh, P. Saxena and M. Kapur *Org. Lett.* 2021, **23**, 8694–8698; (d) Y. Akira; S. Glen; H. Hisashi; T. Masaki; I. Kiyotaka; I. Masashi, WO 2001087845 A2, 2001; (e) Q. Wang and X. Li *Org. Chem. Front.* 2016, **3**, 1159-1162; (f) A. R. Choudhury and S. Mukherjee *Chem. Sci.*, 2016, **7**, 6940-6945.
2. L. Jiang, Z. Wang, M. Armstrong, M. G. Suero, *Angew. Chem., Int. Ed.* 2021, **60**, 6177-6184
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7. G. M. Sheldrick, *Acta Crystallogr. Sect. A* 2008, **64**, 112-122

6. Copies of ^1H , ^{13}C , ^{19}F and ^{31}P NMR Spectra

NRLD-627

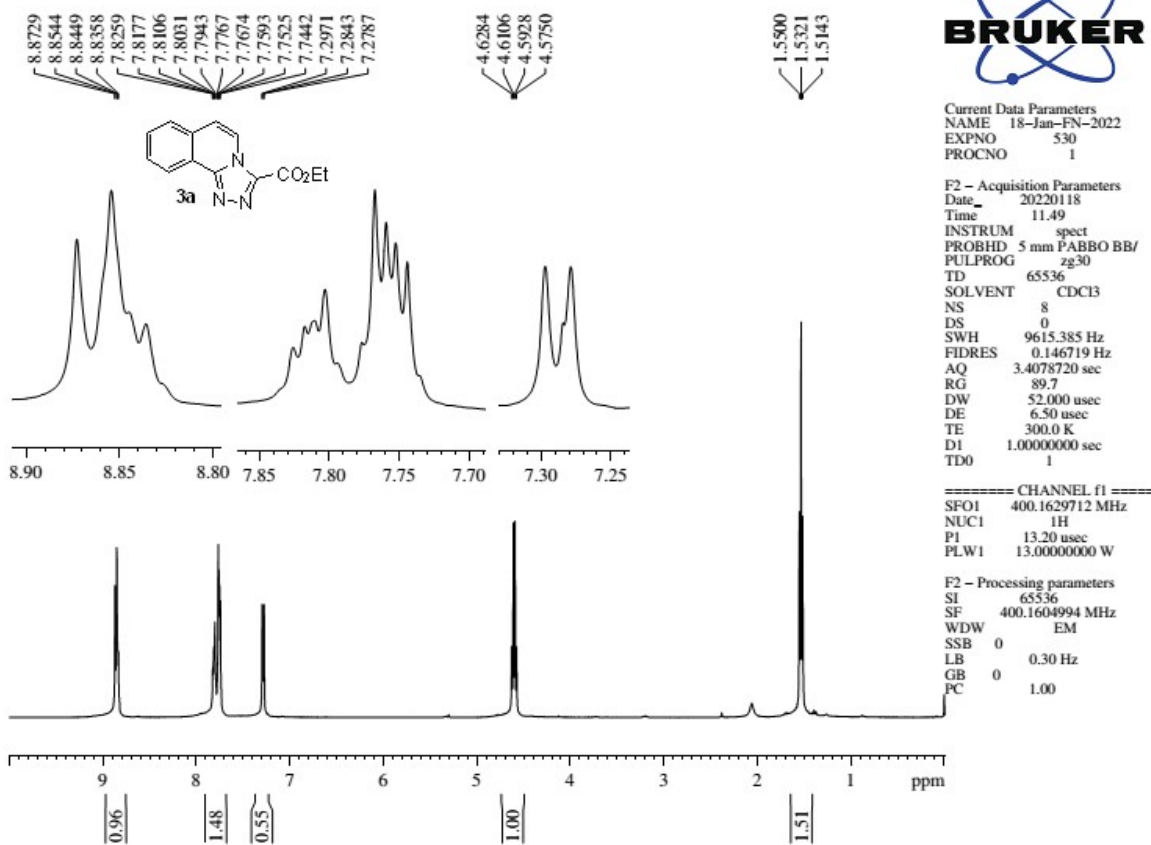


Figure S7: ^1H NMR spectrum of **3a**

NRLD-627

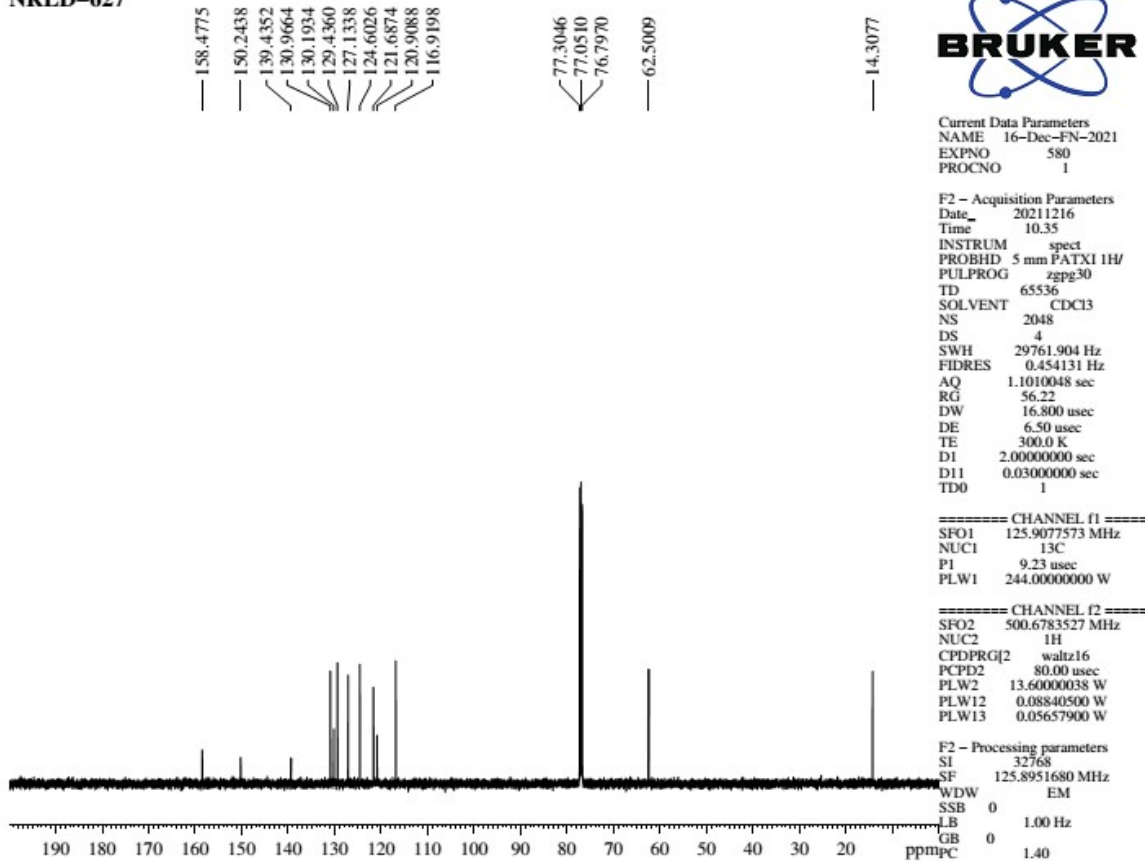


Figure S8: ^{13}C NMR spectrum of **3a**

NRLD-653

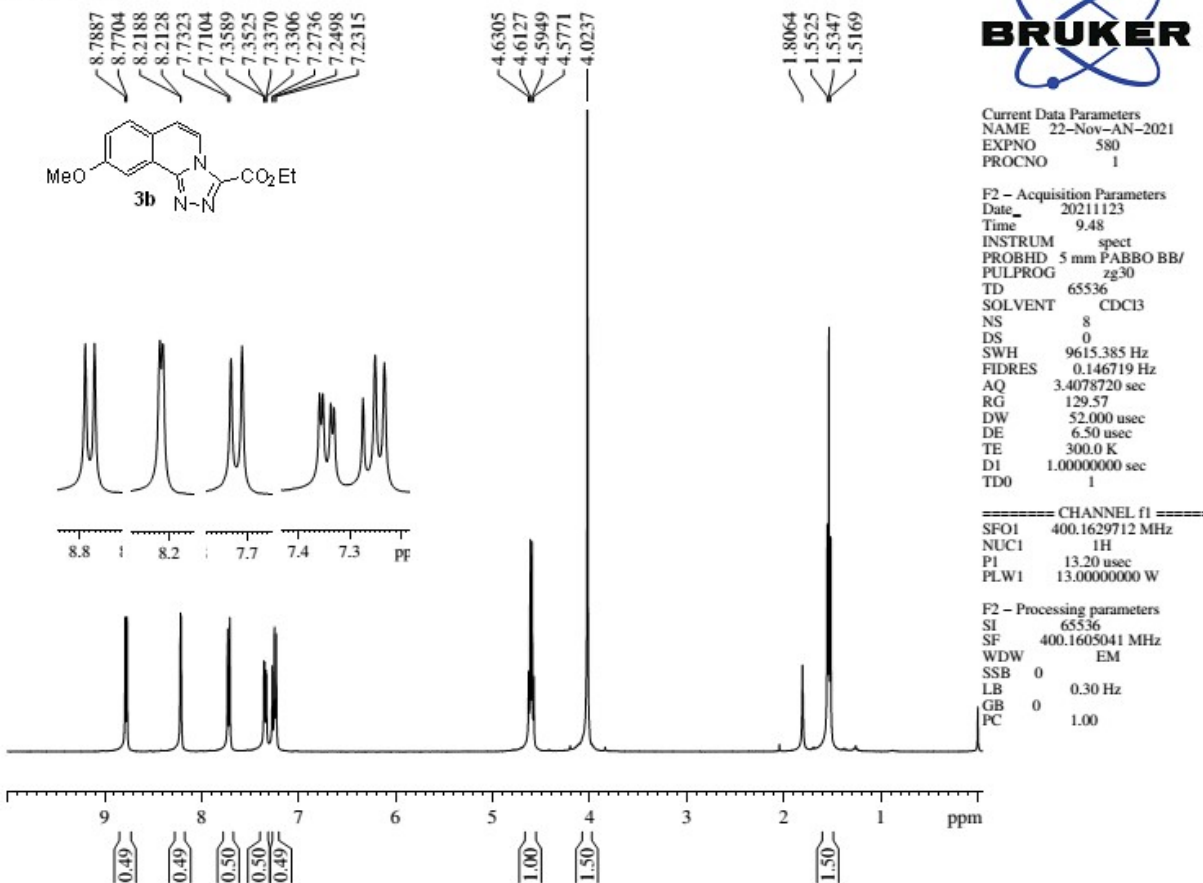


Figure S9: ¹H NMR spectrum of **3b**

NRLD-653

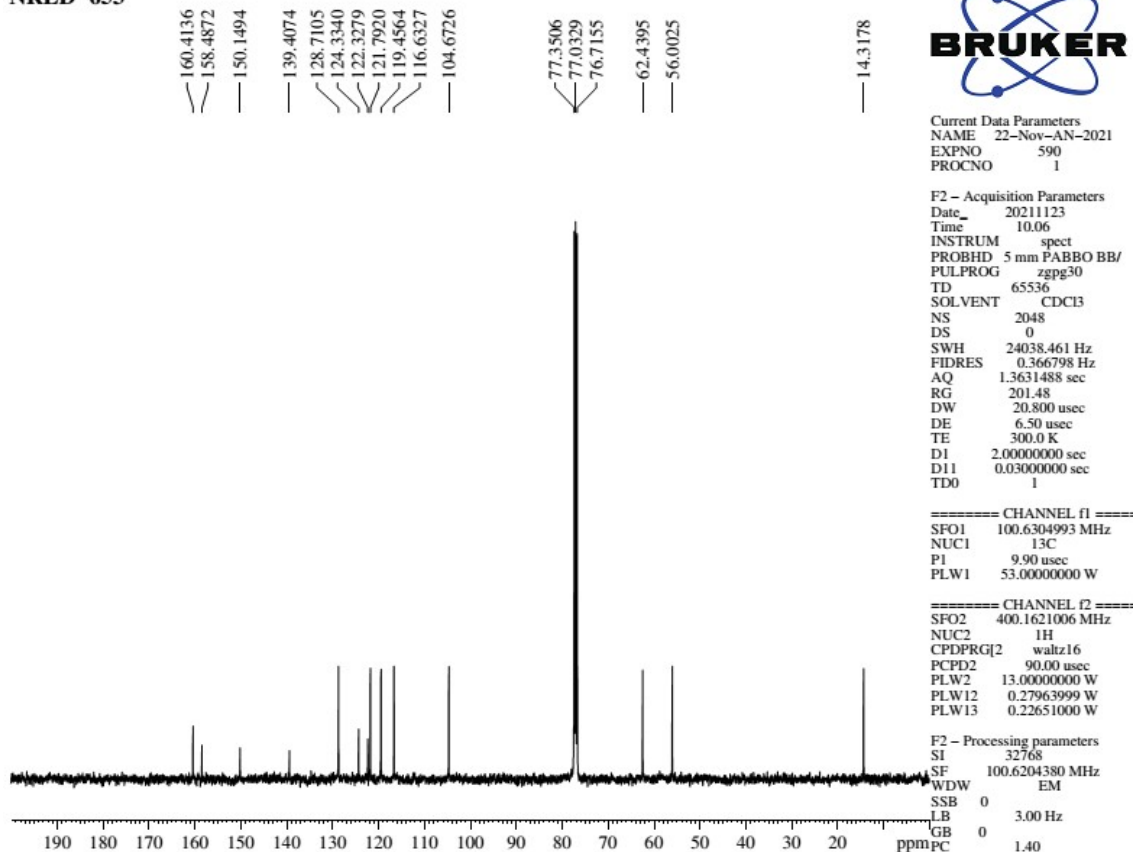
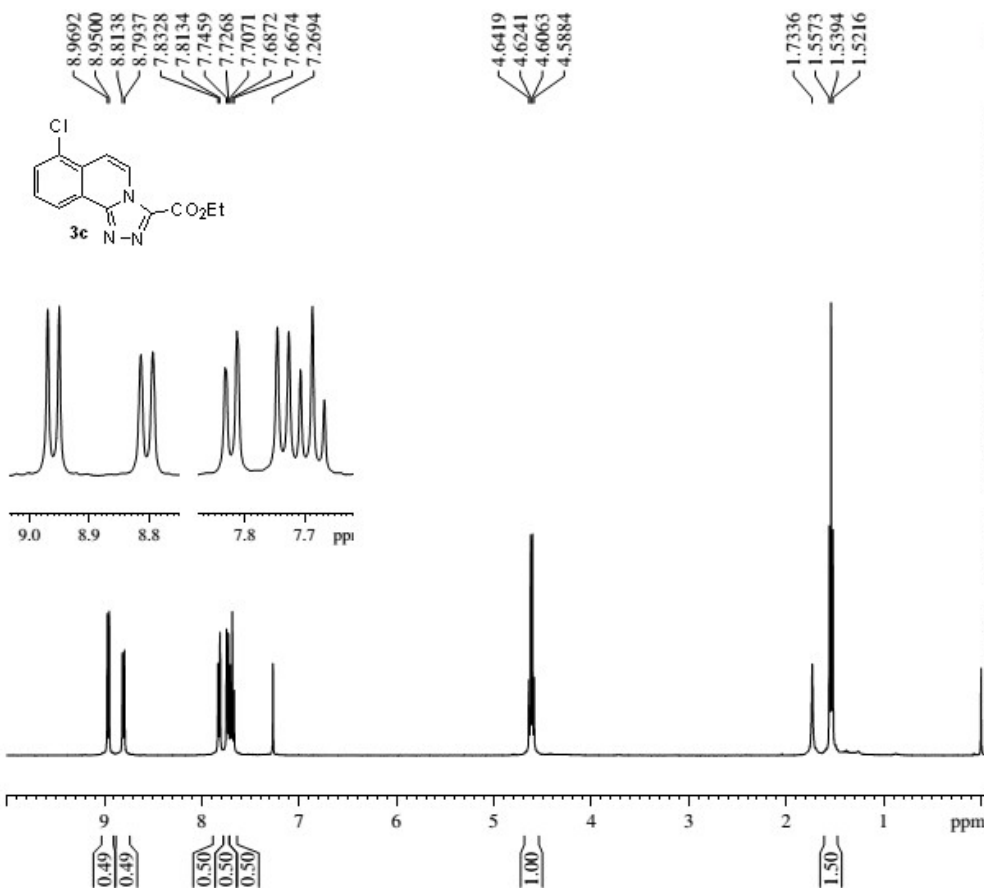


Figure S10: ¹³C NMR spectrum of **3b**

NRLD-638



Current Data Parameters
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 PROCNO 1

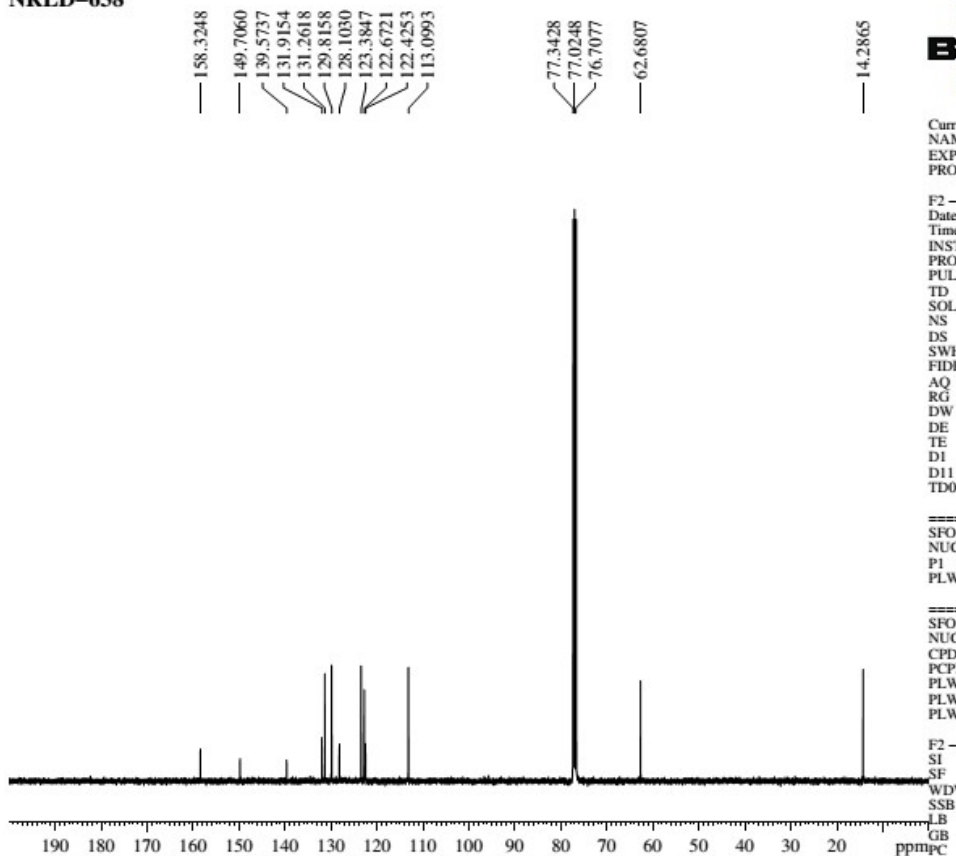
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 Time 7.00
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 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 8
 DS 0
 SWH 9615.385 Hz
 FIDRES 0.146719 Hz
 AQ 3.4078720 sec
 RG 145.29
 DW 52.000 usec
 DE 6.50 usec
 TE 300.0 K
 D1 1.00000000 sec
 TD0 1

==== CHANNEL f1 =====
 SFO1 400.1629712 MHz
 NUC1 1H
 P1 13.20 usec
 PLW1 13.00000000 W

F2 - Processing parameters
 SI 65536
 SF 400.1605057 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

Figure S11: ¹H NMR spectrum of 3c

NRLD-638



Current Data Parameters
 NAME 28-Oct-AN-2021
 EXPNO 520
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20211029
 Time 8.00
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 2048
 DS 0
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631488 sec
 RG 201.48
 DW 20.800 usec
 DE 6.50 usec
 TE 300.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

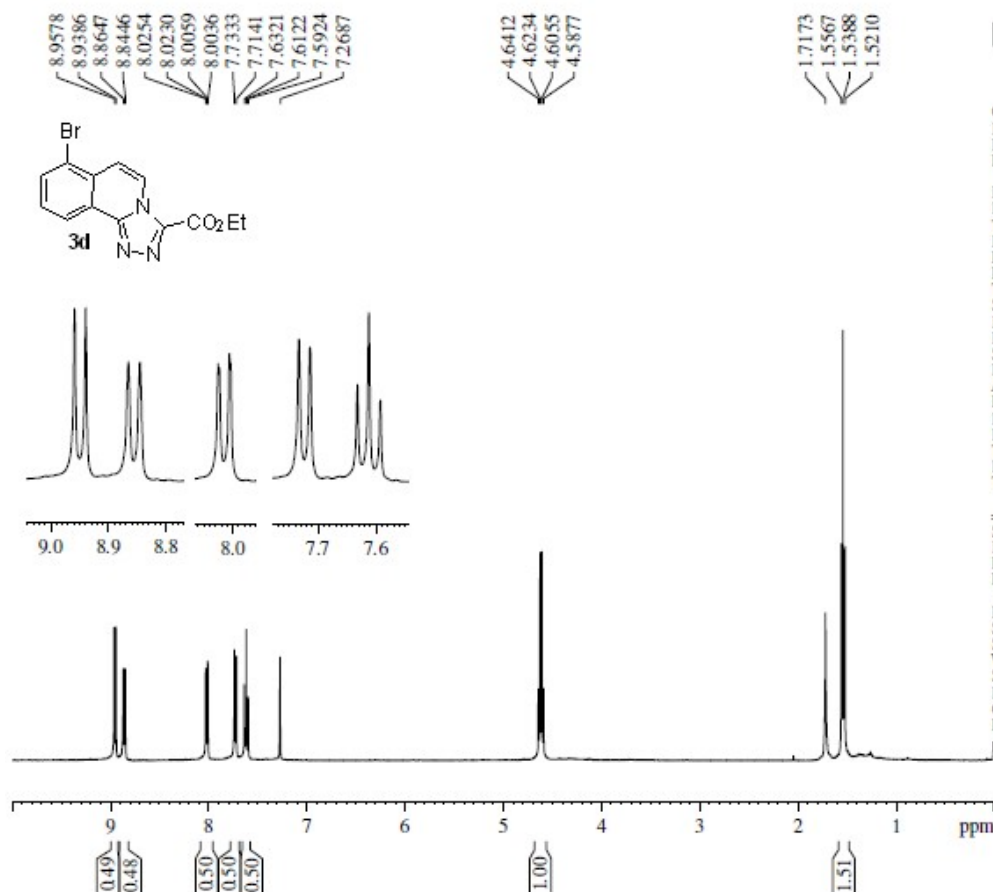
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 NUC1 13C
 P1 9.90 usec
 PLW1 53.00000000 W

==== CHANNEL f2 =====
 SFO2 400.1621006 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 90.00 usec
 PLW2 13.00000000 W
 PLW12 0.27963999 W
 PLW13 0.22651000 W

F2 - Processing parameters
 SI 32768
 SF 100.6204380 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

Figure S12: ¹³C NMR spectrum of 3c

NRPD-634



Current Data Parameters
 NAME 25-Oct-FN-2021
 EXPNO 480
 PROCNO 1

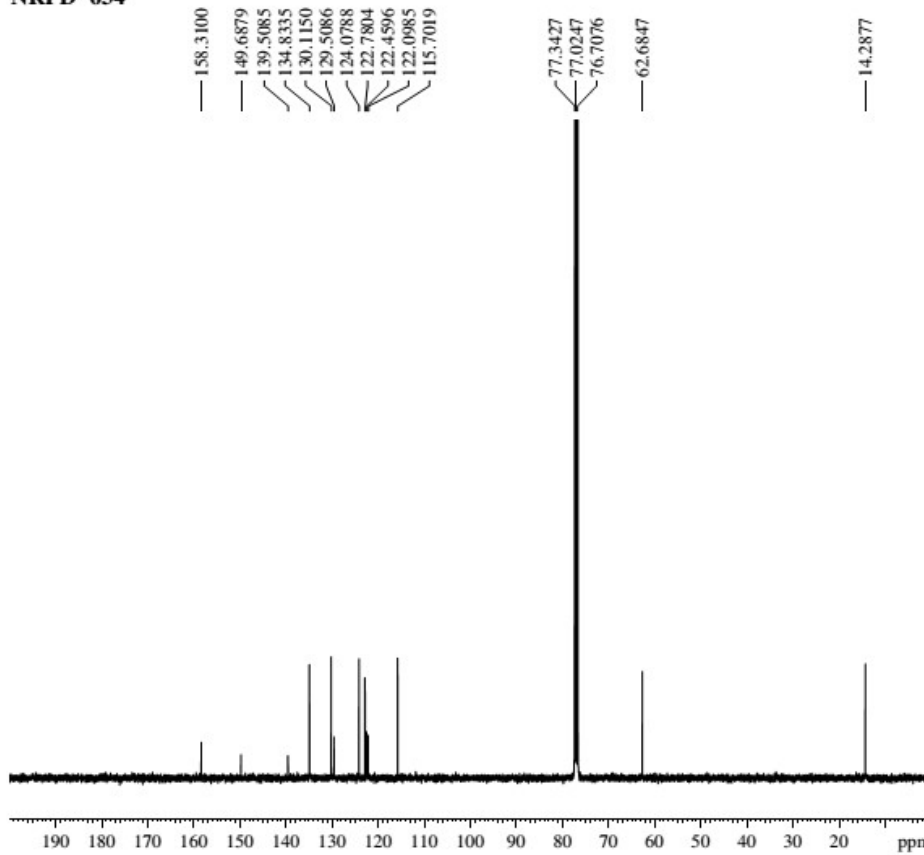
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 Date_ 20211025
 Time 16.44
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 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 8
 DS 0
 SWH 9615.385 Hz
 FIDRES 0.146719 Hz
 AQ 3.4078720 sec
 RG 145.29
 DW 52.000 usec
 DE 6.50 usec
 TE 300.0 K
 D1 1.0000000 sec
 TD0 1

==== CHANNEL f1 ====
 SFO1 400.1629712 MHz
 NUC1 1H
 P1 13.20 usec
 PLW1 13.00000000 W

F2 - Processing parameters
 SI 65336
 SF 400.1605061 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

Figure S13: ¹H NMR spectrum of 3d

NRPD-634



Current Data Parameters
 NAME 25-Oct-FN-2021
 EXPNO 490
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20211025
 Time 16.49
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 2048
 DS 0
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631488 sec
 RG 201.48
 DW 20.800 usec
 DE 6.50 usec
 TE 300.0 K
 D1 2.0000000 sec
 D11 0.03000000 sec
 TD0 1

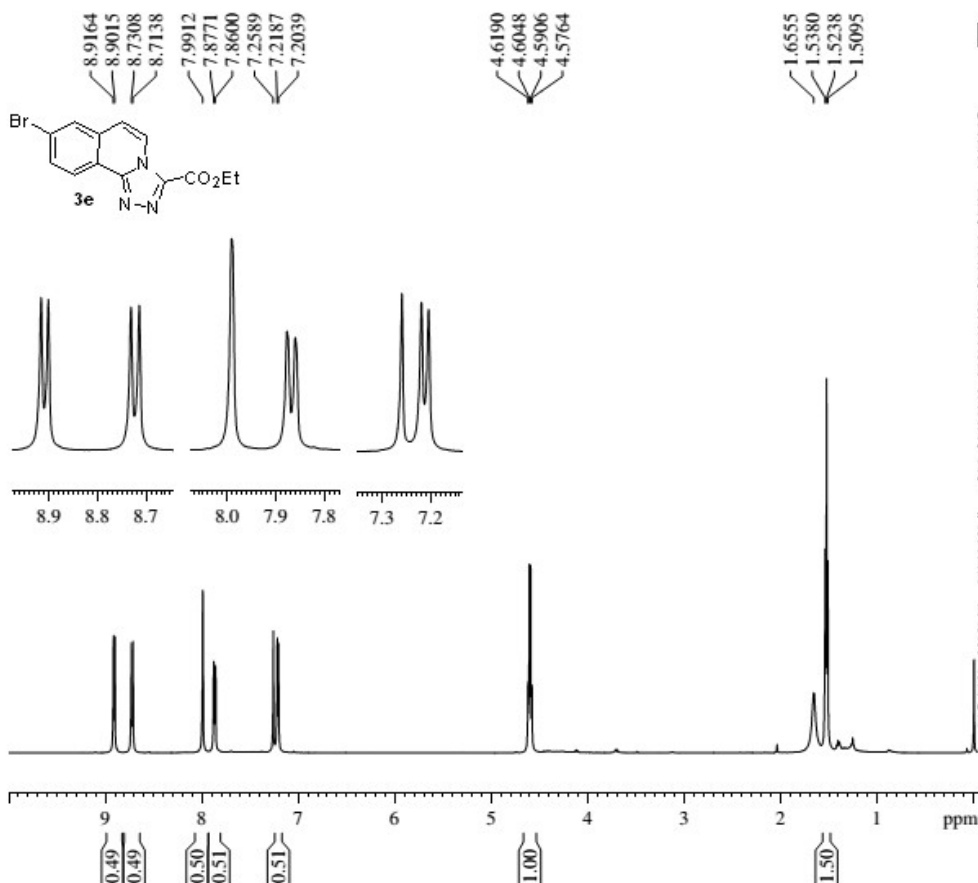
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 NUC1 13C
 P1 9.90 usec
 PLW1 53.00000000 W

==== CHANNEL f2 ====
 SFO2 400.1621006 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 90.00 usec
 PLW2 13.00000000 W
 PLW12 0.27963999 W
 PLW13 0.22651000 W

F2 - Processing parameters
 SI 32768
 SF 100.6204380 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

Figure S14: ¹³C NMR spectrum of 3d

NRLD-635



Current Data Parameters
 NAME 26-Oct-AN-2021
 EXPNO 450
 PROCNO 1

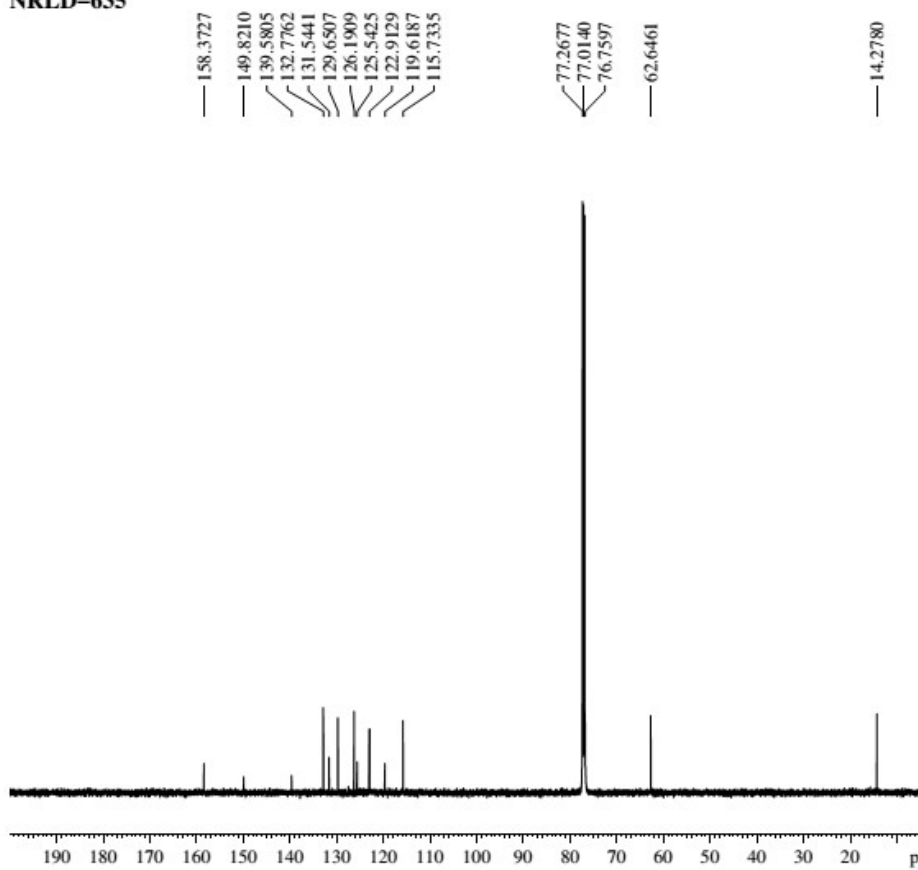
F2 - Acquisition Parameters
 Date_ 20211026
 Time 17.32
 INSTRUM spect
 PROBHD 5 mm PATXI 1H/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 10026.738 Hz
 FIDRES 0.152996 Hz
 AQ 3.2680619 sec
 RG 201.78
 DW 49.867 usec
 DE 6.50 usec
 TE 303.0 K
 D1 1.00000000 sec
 TD0 1

==== CHANNEL f1 =====
 SFO1 500.6794419 MHz
 NUC1 1H
 P1 6.45 usec
 PLW1 13.60000038 W

F2 - Processing parameters
 SI 65536
 SF 500.6763620 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

Figure S15: ¹H NMR spectrum of 3e

NRLD-635



Current Data Parameters
 NAME 26-Oct-AN-2021
 EXPNO 460
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20211026
 Time 17.30
 INSTRUM spect
 PROBHD 5 mm PATXI 1H/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 4096
 DS 4
 SWH 29761.904 Hz
 FIDRES 0.454131 Hz
 AQ 1.1010048 sec
 RG 56.22
 DW 16.800 usec
 DE 6.50 usec
 TE 303.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

==== CHANNEL f1 =====
 SFO1 125.9077573 MHz
 NUC1 13C
 P1 9.23 usec
 PLW1 244.00000000 W

==== CHANNEL f2 =====
 SFO2 500.6783527 MHz
 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 80.00 usec
 PLW2 13.60000038 W
 PLW12 0.08840500 W
 PLW13 0.05657900 W

F2 - Processing parameters
 SI 32768
 SF 125.8951680 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

Figure S16: ¹³C NMR spectrum of 3e

NRLD-656

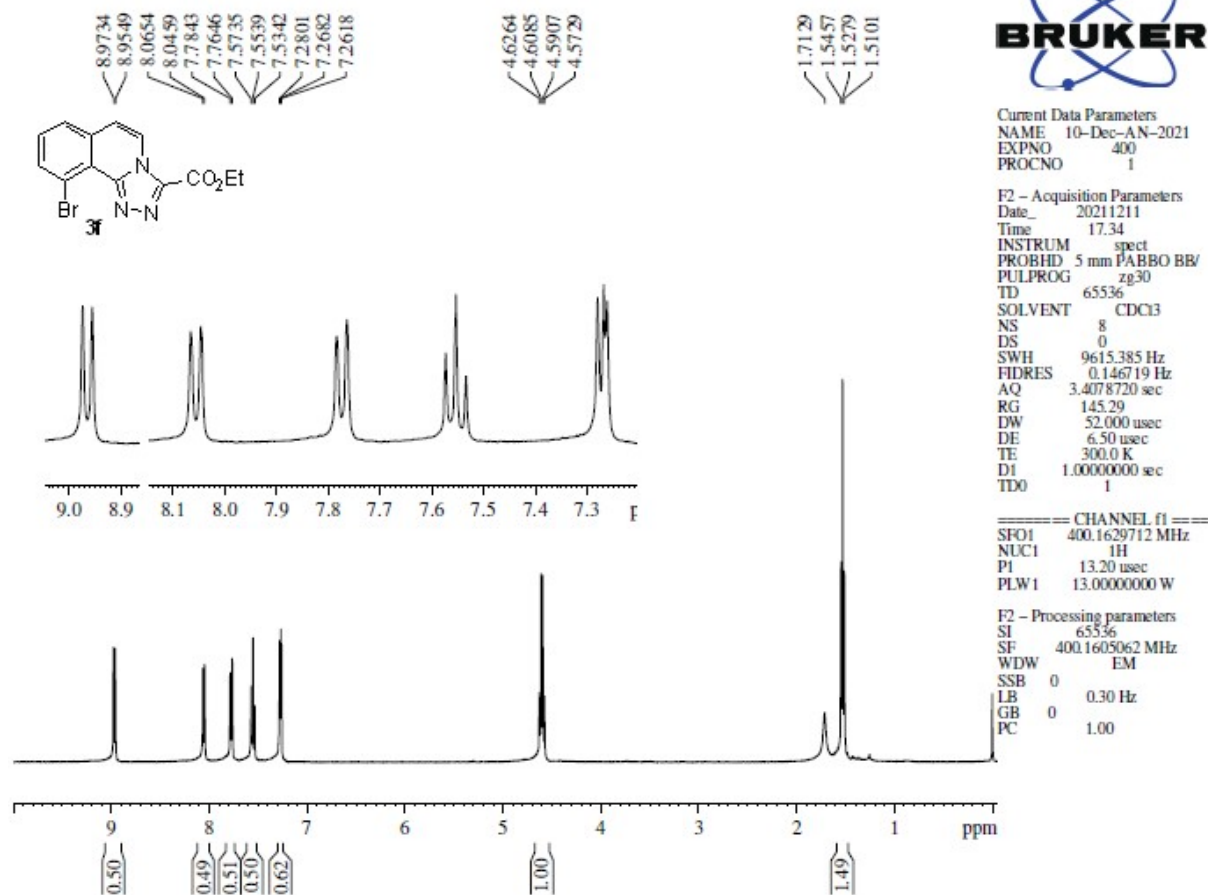


Figure S17: ¹H NMR spectrum of 3f

NRLD-656

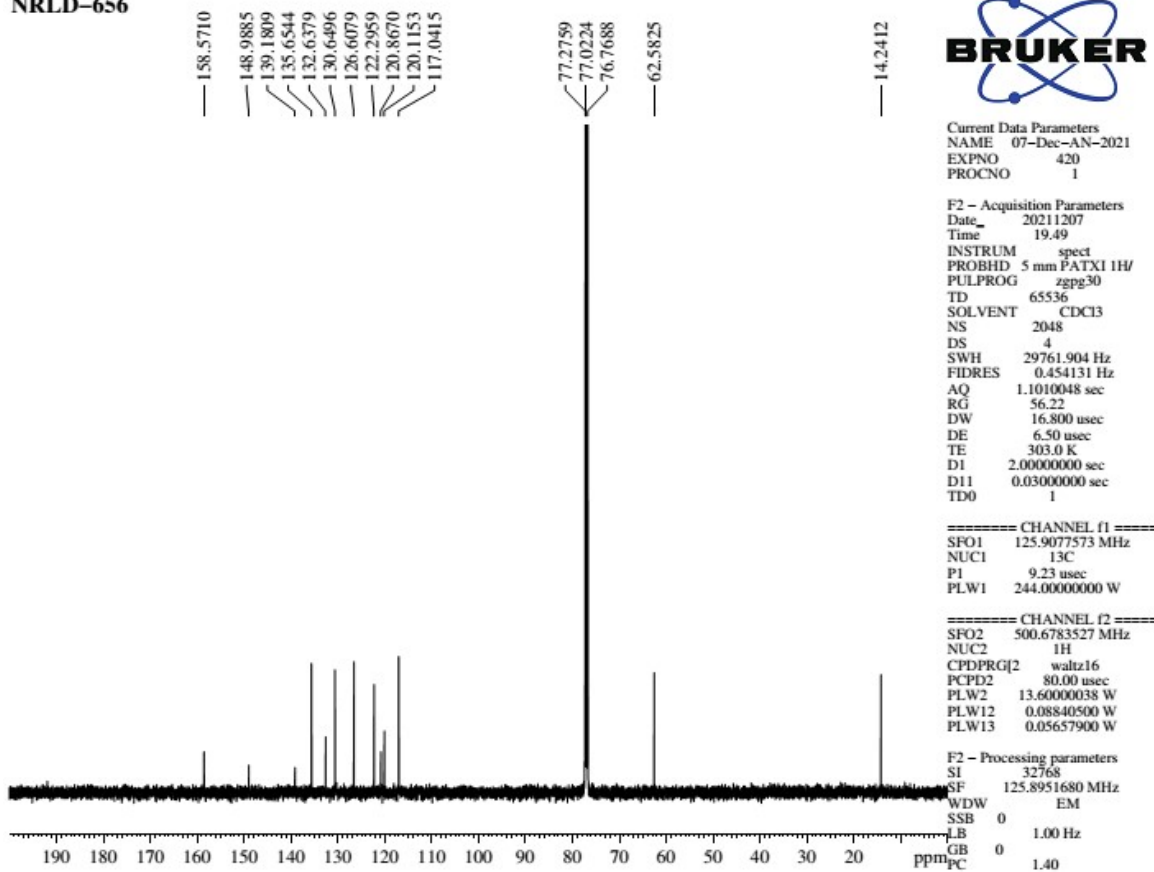
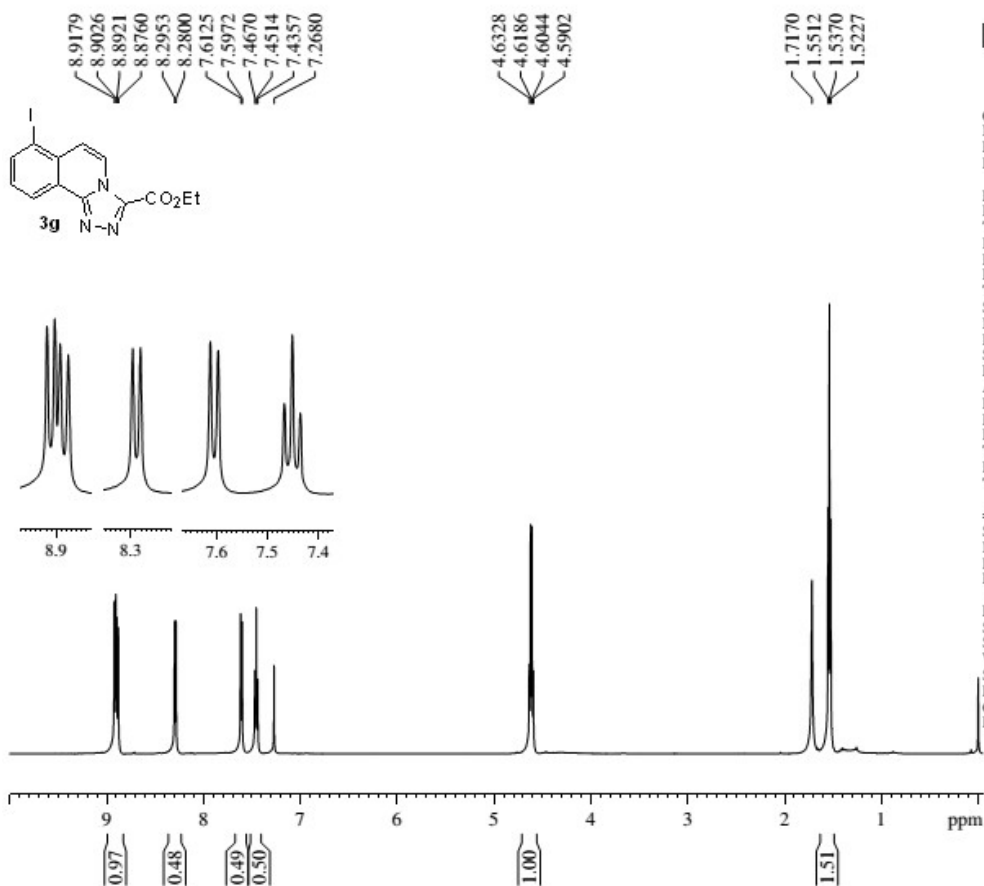


Figure S18: ¹³C NMR spectrum of 3f

NRLD-639



Current Data Parameters
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 PROCNO 1

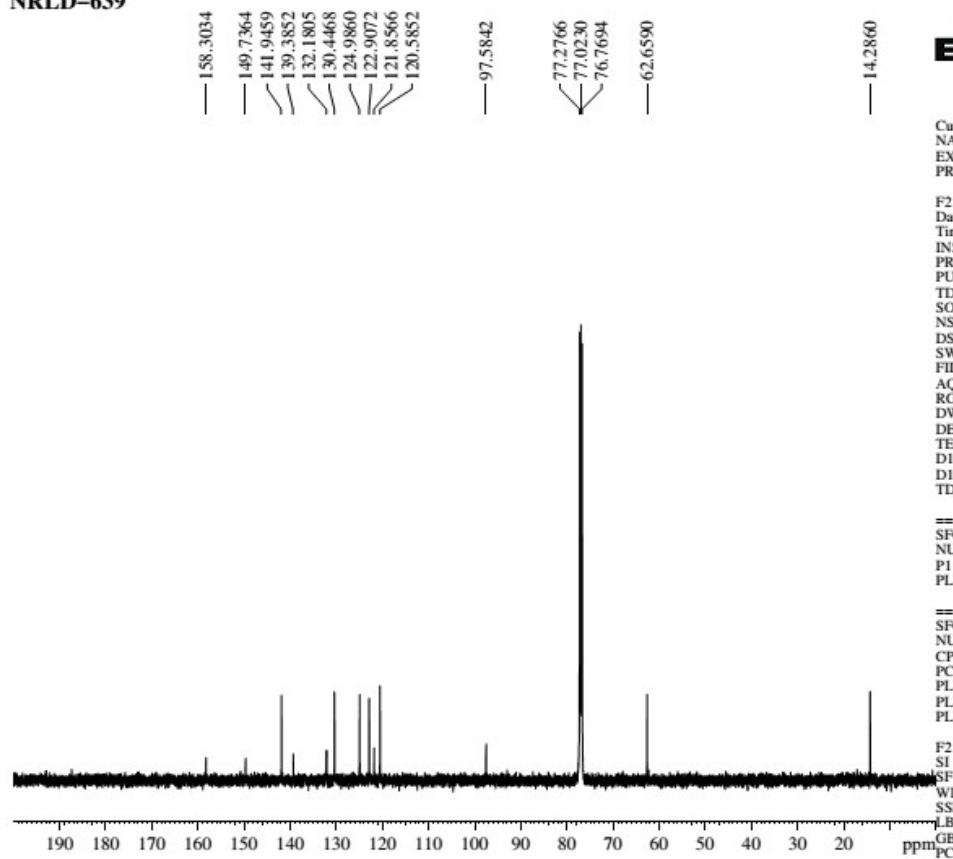
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 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 10026.738 Hz
 FIDRES 0.152996 Hz
 AQ 3.2680619 sec
 RG 201.78
 DW 49.867 usec
 DE 6.50 usec
 TE 303.0 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 SFO1 500.6794419 MHz
 NUC1 1H
 P1 6.45 usec
 PLW1 13.60000038 W

F2 - Processing parameters
 SI 65536
 SF 500.6763578 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

Figure S19: ¹H NMR spectrum of **3g**

NRLD-639



Current Data Parameters
 NAME 01-Nov-FN-2021
 EXPNO 550
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20211101
 Time 10.44
 INSTRUM spect
 PROBHD 5 mm PATXI 1H/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1500
 DS 4
 SWH 29761.904 Hz
 FIDRES 0.454131 Hz
 AQ 1.1010048 sec
 RG 56.22
 DW 16.800 usec
 DE 6.50 usec
 TE 303.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

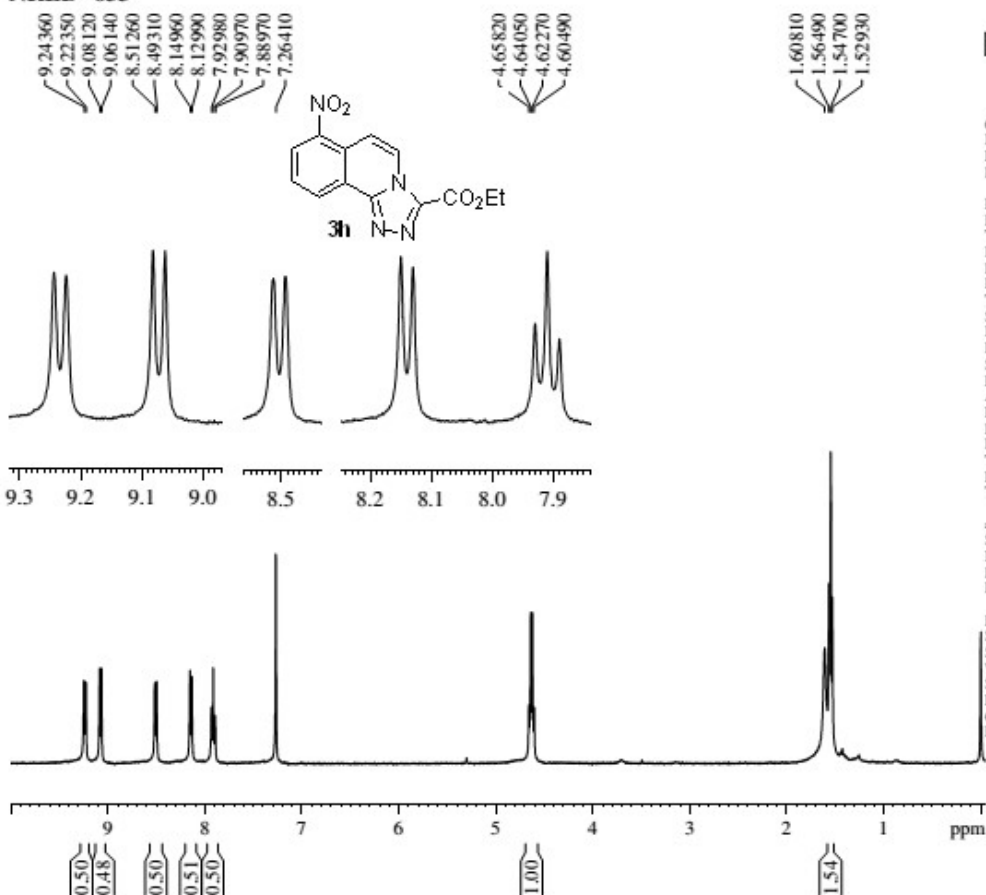
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 SFO1 125.9077573 MHz
 NUC1 13C
 P1 9.23 usec
 PLW1 244.00000000 W

===== CHANNEL f2 =====
 SFO2 500.6783527 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 80.00 usec
 PLW2 13.60000038 W
 PLW12 0.08840500 W
 PLW13 0.05657900 W

F2 - Processing parameters
 SI 32768
 SF 125.8951680 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

Figure S20: ¹³C NMR spectrum of **3g**

NRLD-633



Current Data Parameters
 NAME 29-Dec-AN-2021
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 PROCNO 1

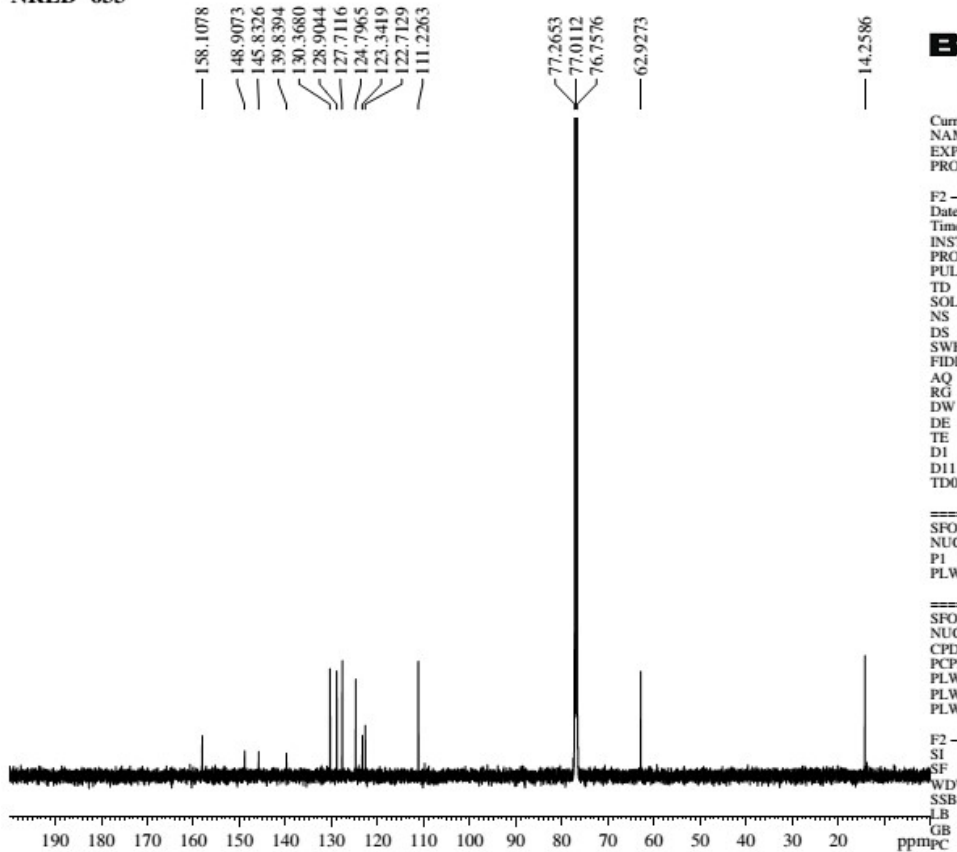
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 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 8
 DS 0
 SWH 9615.385 Hz
 FIDRES 0.146719 Hz
 AQ 3.4078720 sec
 RG 179.93
 DW 52.000 usec
 DE 6.50 usec
 TE 300.0 K
 D1 1.00000000 sec
 TD0 1

==== CHANNEL f1 =====
 SFO1 400.1629712 MHz
 NUC1 1H
 P1 13.20 usec
 PLW1 13.00000000 W

F2 - Processing parameters
 SI 65536
 SF 400.1605079 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

Figure S21: ¹H NMR spectrum of 3h

NRLD-633



Current Data Parameters
 NAME 10-Nov-FN-2021
 EXPNO 500
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20211111
 Time 0.47
 INSTRUM spect
 PROBHD 5 mm PATXI 1H/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 4096
 DS 4
 SWH 29761.904 Hz
 FIDRES 0.454131 Hz
 AQ 1.1010048 sec
 RG 56.22
 DW 16.800 usec
 DE 6.50 usec
 TE 303.0 K
 D1 2.0000000 sec
 D11 0.03000000 sec
 TD0 1

==== CHANNEL f1 =====
 SFO1 125.9077573 MHz
 NUC1 13C
 P1 9.23 usec
 PLW1 244.00000000 W

==== CHANNEL f2 =====
 SFO2 500.6783527 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 80.00 usec
 PLW2 13.60000038 W
 PLW12 0.08840500 W
 PLW13 0.05657900 W

F2 - Processing parameters
 SI 32768
 SF 125.8951680 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

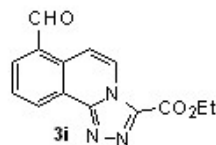
Figure S22: ¹³C NMR spectrum of 3h

NRLD-649

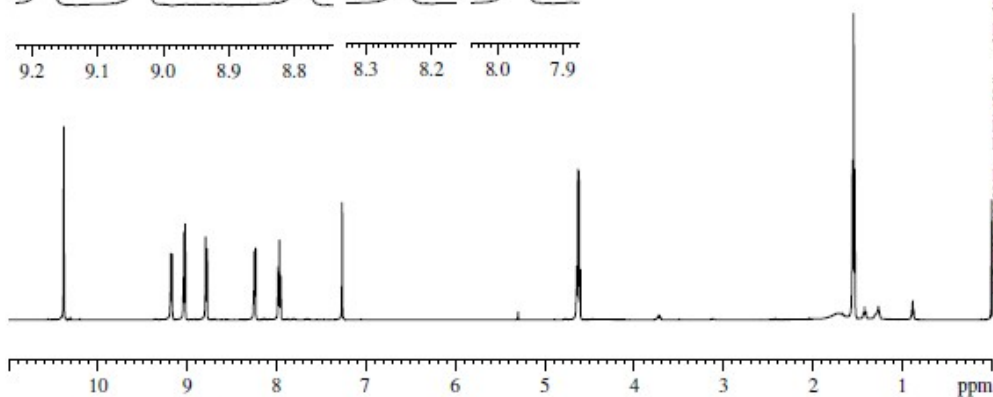
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9.0402
9.0247
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8.2528
8.2506
8.2381
8.2359
7.9849
7.9693
7.9603
7.9541
7.2665

4.6446
4.6303
4.6160
4.6018

1.5572
1.5430
1.5287



9.2 9.1 9.0 8.9 8.8 8.3 8.2 8.0 7.9



0.49 0.49 0.49 0.50 0.50 1.00 1.51



Current Data Parameters
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EXPNO 530
PROCNO 1

F2 - Acquisition Parameters
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TD 65536
SOLVENT CDCl3
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DS 2
SWH 10026.738 Hz
FIDRES 0.152996 Hz
AQ 3.2680619 sec
RG 201.78
DW 49.867 usec
DE 6.50 usec
TE 303.0 K
D1 1.00000000 sec
TD0 1

==== CHANNEL f1 ====
SFO1 500.6794419 MHz
NUC1 1H
P1 6.45 usec
PLW1 13.60000038 W

F2 - Processing parameters
SI 65536
SF 500.6763582 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Figure S23: ¹H NMR spectrum of 3i

NRLD-649

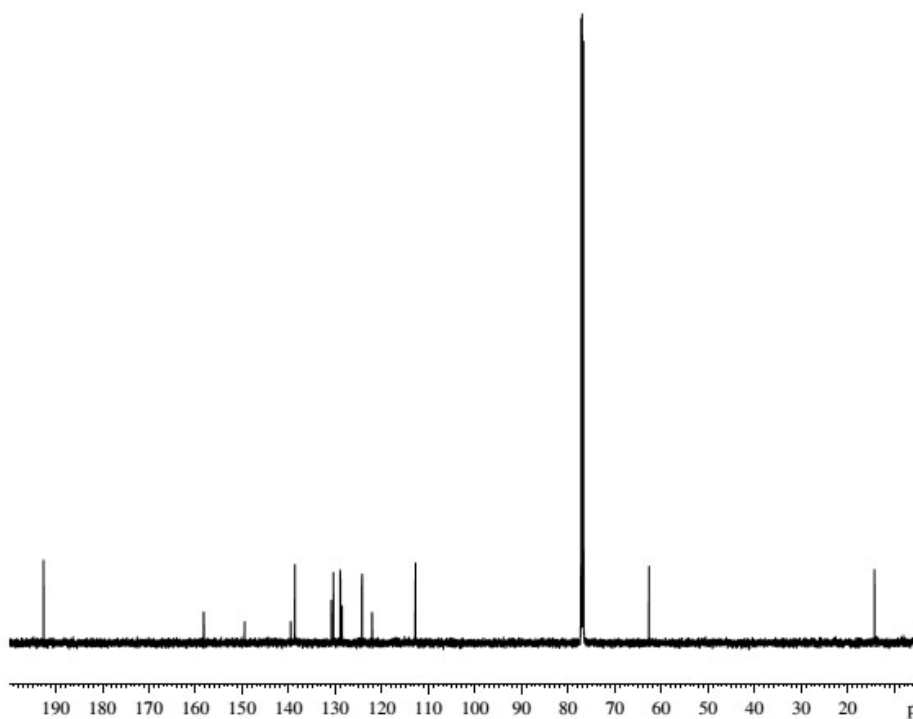
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128.5707
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112.8457

77.2686
77.0150
76.7613

62.7111

14.2824



Current Data Parameters
NAME 17-Nov-AN-2021
EXPNO 520
PROCNO 1

F2 - Acquisition Parameters
Date_ 20211117
Time 21.21
INSTRUM spect
PROBHD 5 mm PATX1 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 56.22
DW 16.800 usec
DE 6.50 usec
TE 303.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

==== CHANNEL f1 ====
SFO1 125.9077573 MHz
NUC1 13C
P1 9.23 usec
PLW1 244.00000000 W

==== CHANNEL f2 ====
SFO2 500.6783527 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 80.00 usec
PLW2 13.60000038 W
PLW12 0.08840500 W
PLW13 0.05657900 W

F2 - Processing parameters
SI 32768
SF 125.8951680 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Figure S24: ¹³C NMR spectrum of 3i

NRLD-91P

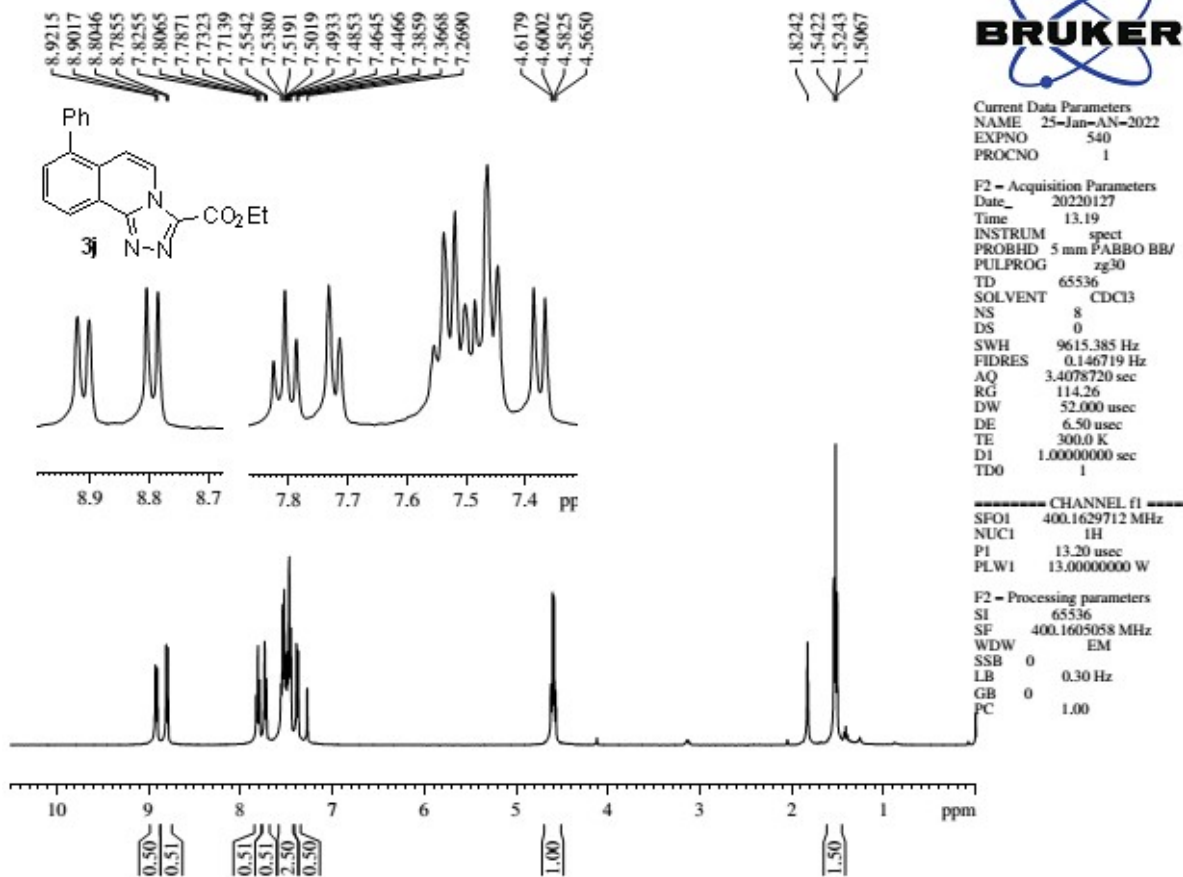


Figure S25: ¹H NMR spectrum of **3j**

NRLD-91P

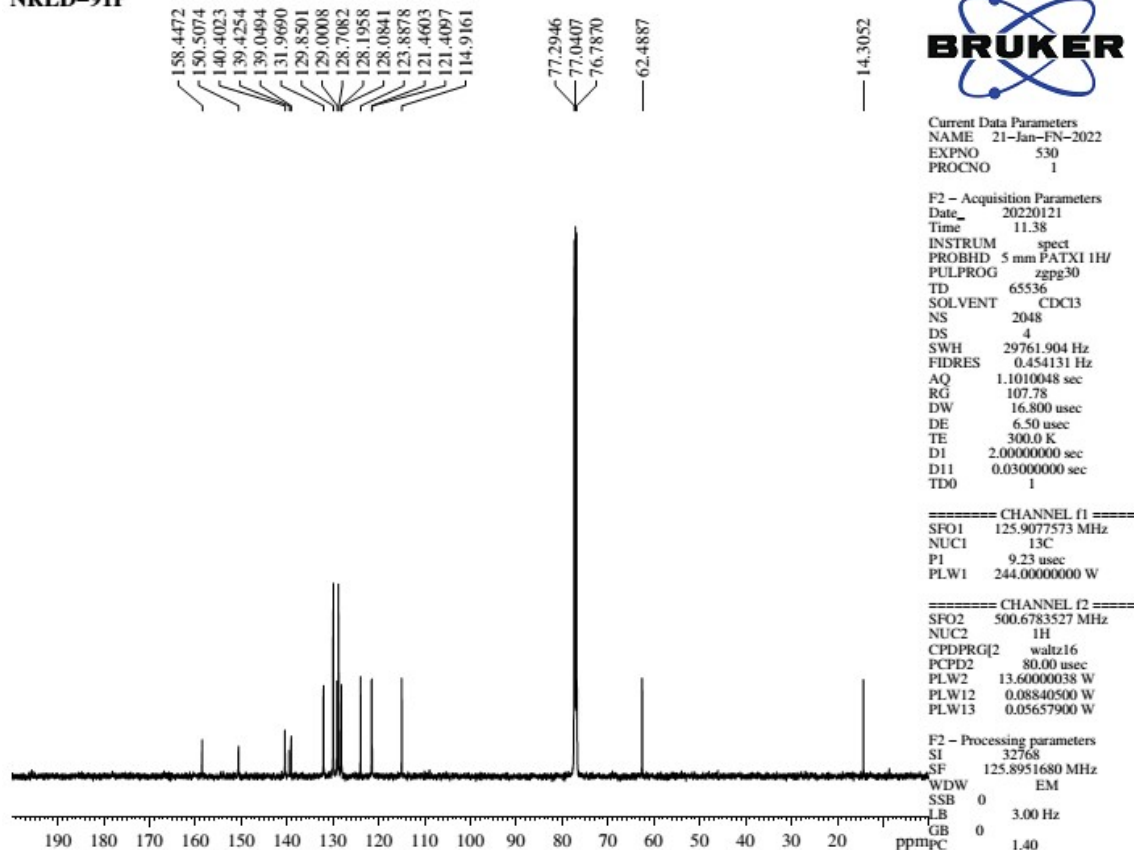


Figure S26: ¹³C NMR spectrum of **3j**

NRLD-661

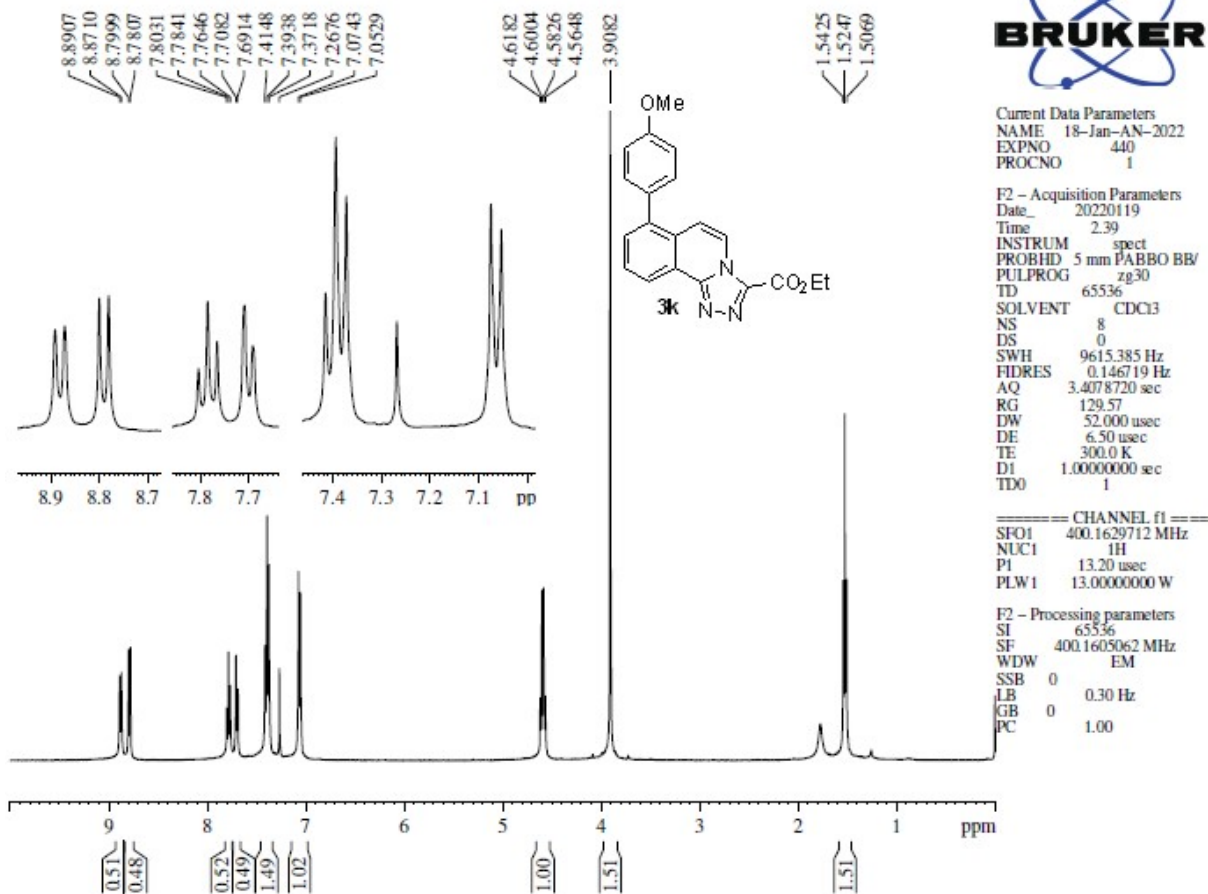


Figure S27: ¹H NMR spectrum of 3k

NRLD-661

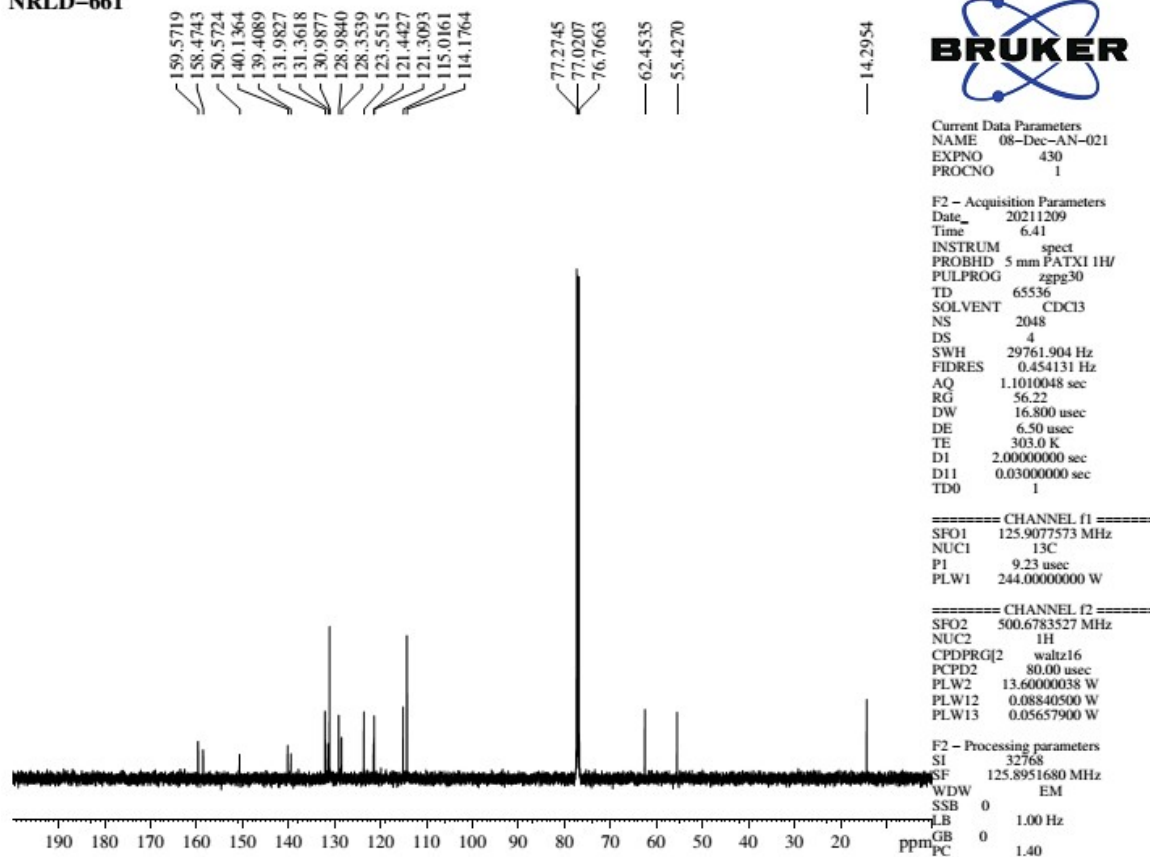
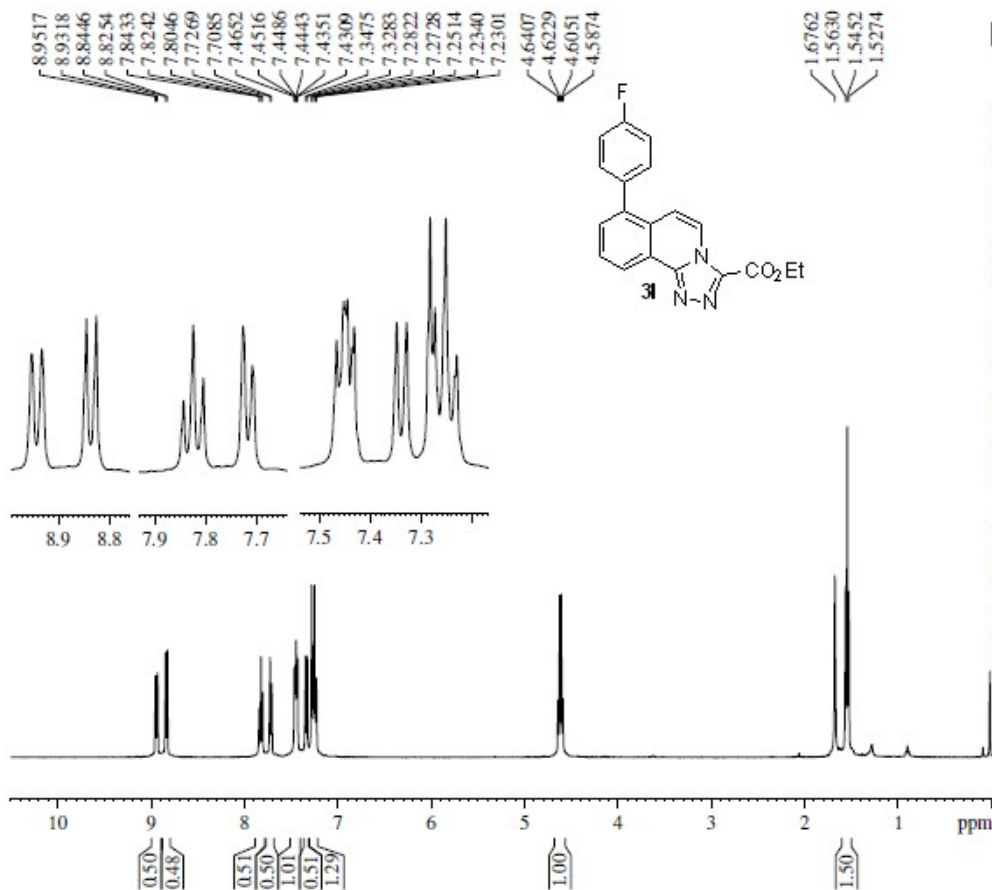


Figure S28: ¹³C NMR spectrum of 3k

NRLD-687



Current Data Parameters
 NAME 10-Feb-AN-2022
 EXPNO 310
 PROCNO 1

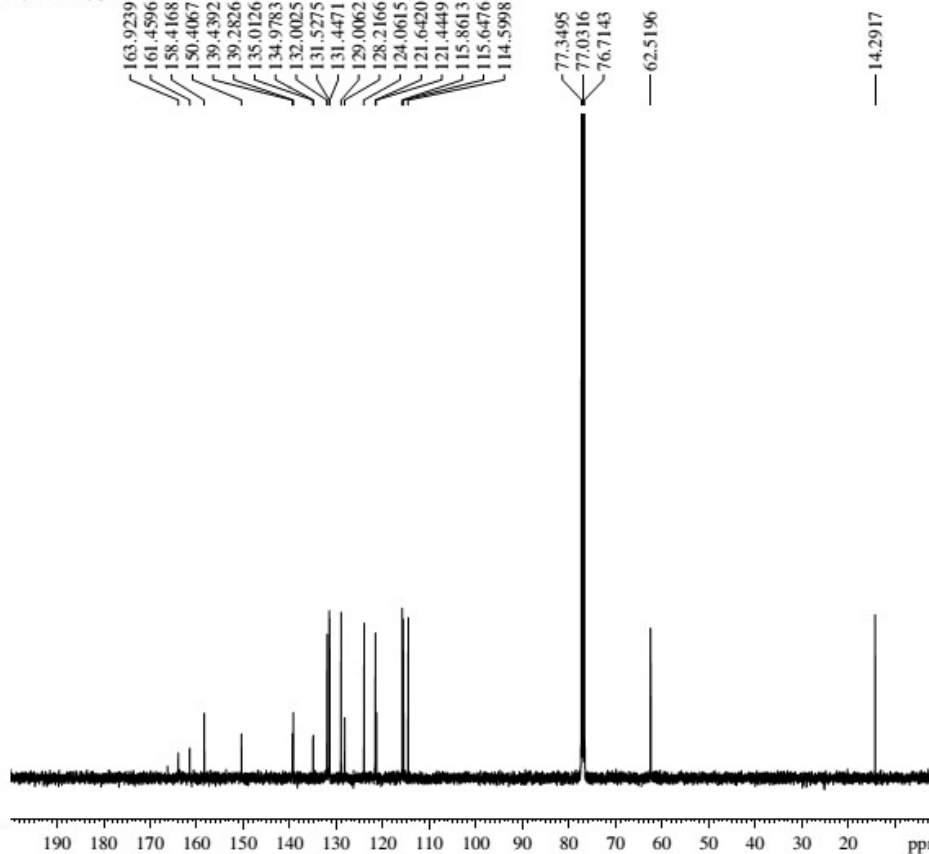
F2 - Acquisition Parameters
 Date_ 20220211
 Time 11.35
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 8
 DS 4
 SWH 9615.385 Hz
 FIDRES 0.146719 Hz
 AQ 3.4078720 sec
 RG 201.48
 DW 52.000 usec
 DE 6.50 usec
 TE 300.0 K
 D1 1.00000000 sec
 TD0 1

==== CHANNEL f1 ====
 SFO1 400.1629712 MHz
 NUC1 1H
 P1 13.20 usec
 PLW1 13.00000000 W

F2 - Processing parameters
 SI 65536
 SF 400.1605000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

Figure S29: ¹H NMR spectrum of **3l**

NRLD 687



Current Data Parameters
 NAME 20-Jan-FN-2022
 EXPNO 420
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20220121
 Time 3.51
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 2048
 DS 0
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631488 sec
 RG 201.48
 DW 20.800 usec
 DE 6.50 usec
 TE 300.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

==== CHANNEL f1 ====
 SFO1 100.6304993 MHz
 NUC1 13C
 P1 9.90 usec
 PLW1 53.00000000 W

==== CHANNEL f2 ====
 SFO2 400.1621006 MHz
 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 90.00 usec
 PLW2 13.00000000 W
 PLW12 0.27963999 W
 PLW13 0.22651000 W

F2 - Processing parameters
 SI 32768
 SF 100.6204380 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

Figure S30: ¹³C NMR spectrum of **3l**

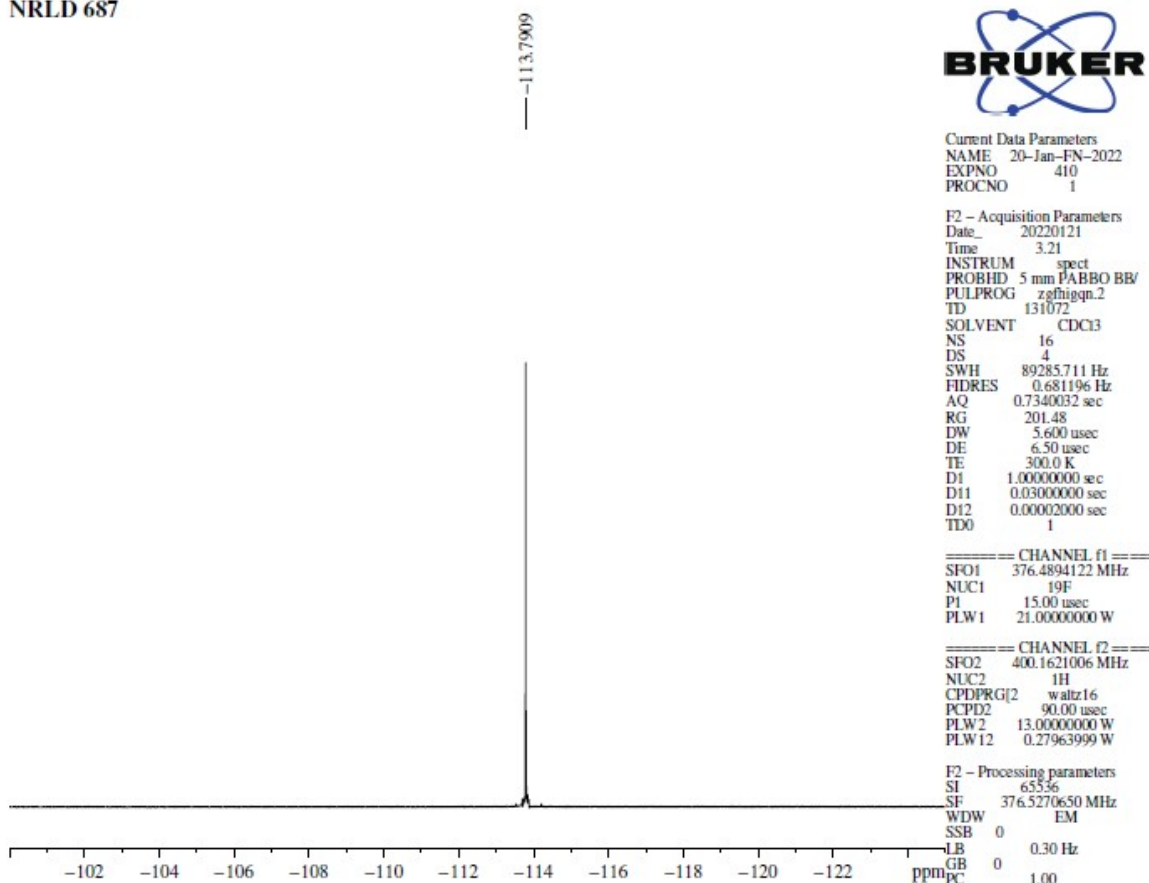


Figure S31: ¹⁹F NMR spectrum of 3l

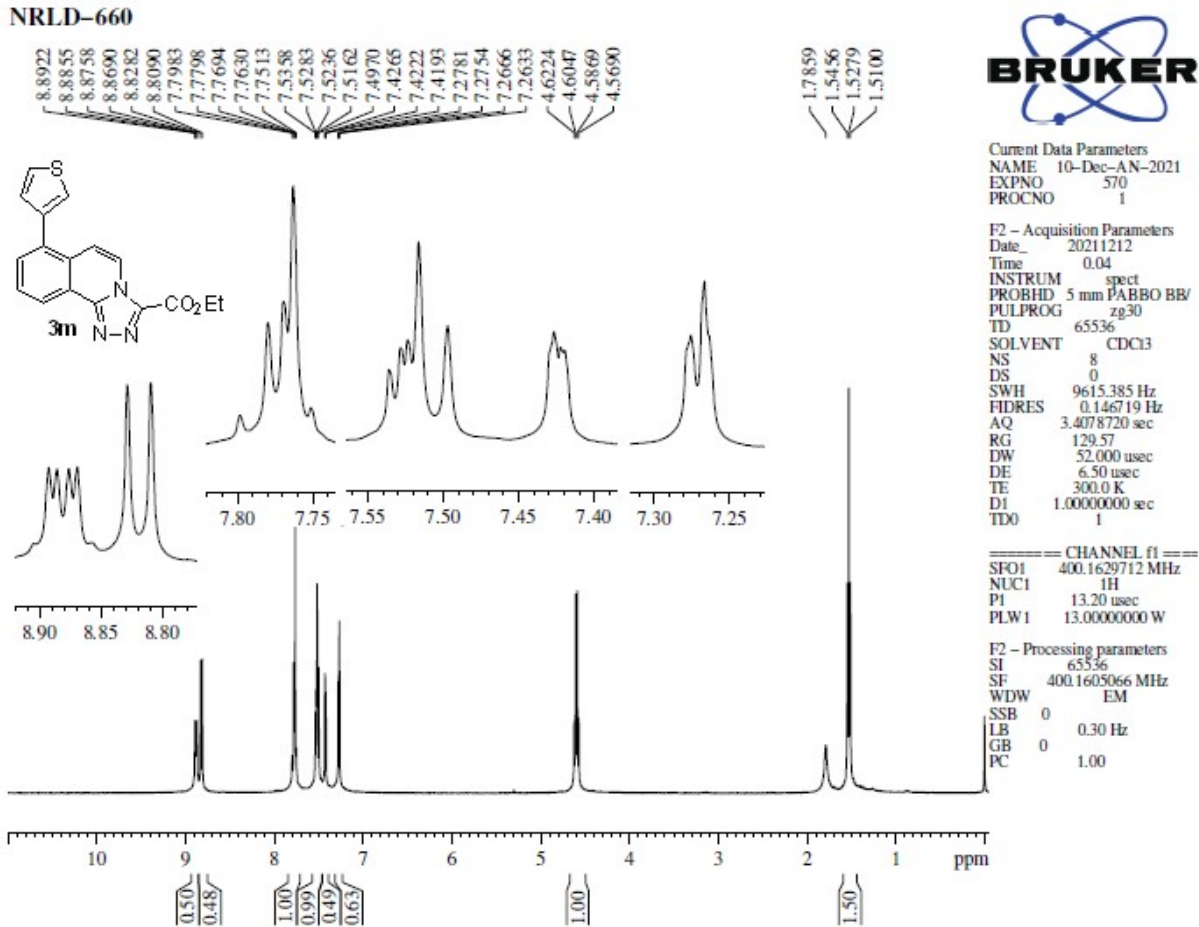


Figure S32: ¹H NMR spectrum of 3m

NRLD-660

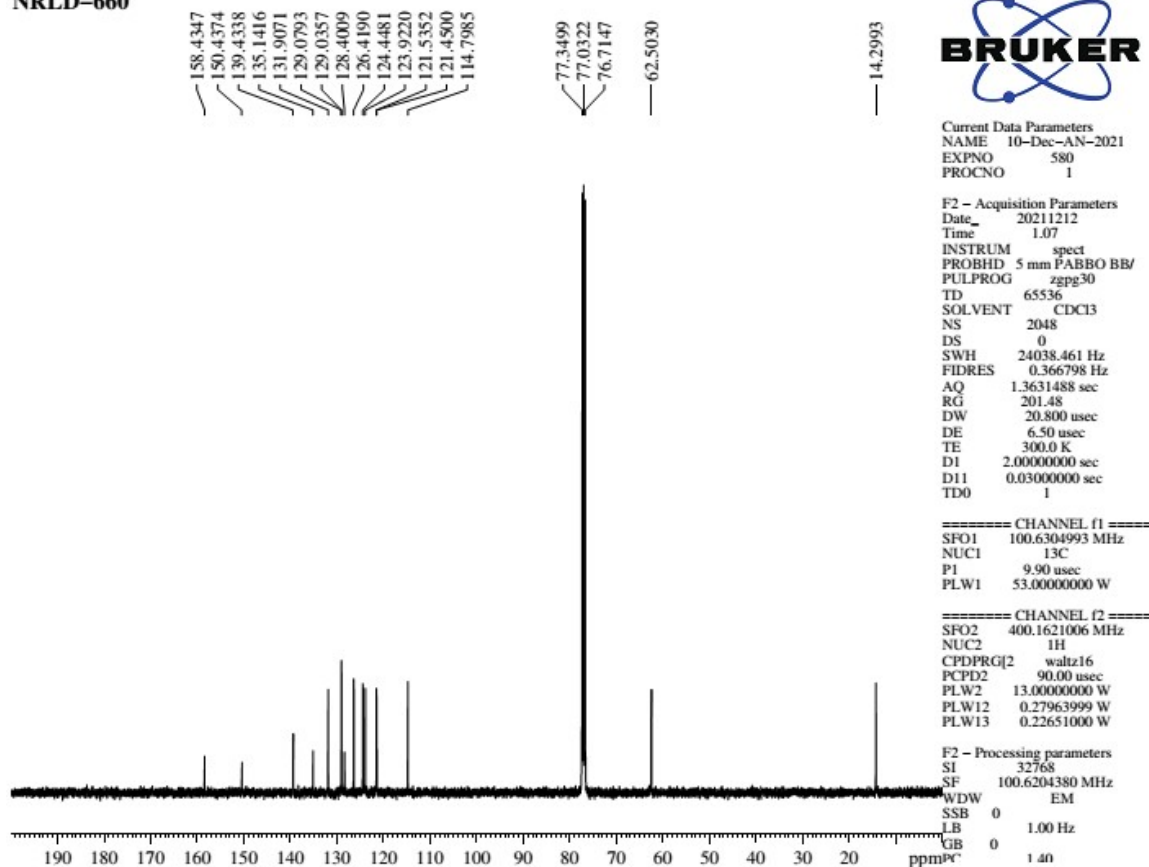


Figure S33: ¹³C NMR spectrum of 3m

NRLD-651

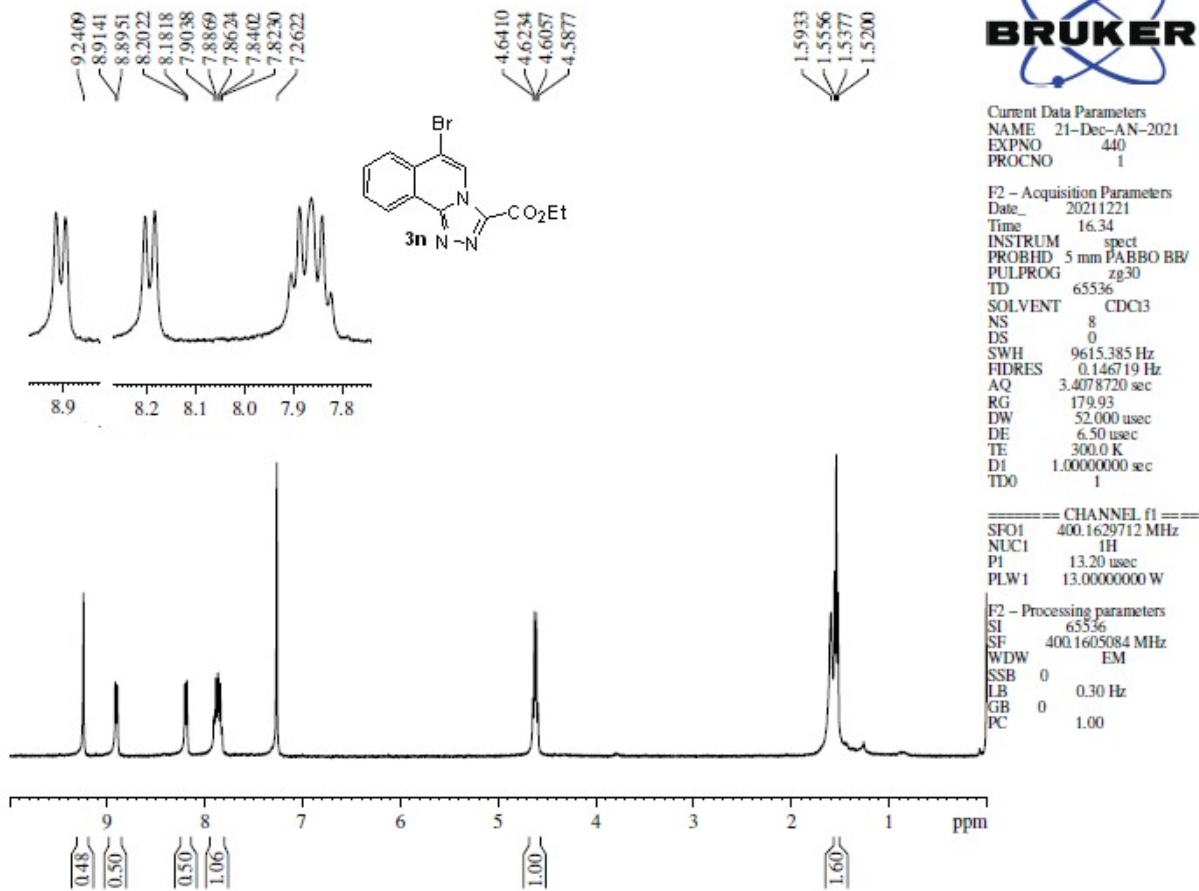


Figure S34: ¹H NMR spectrum of 3n

NRLD-651

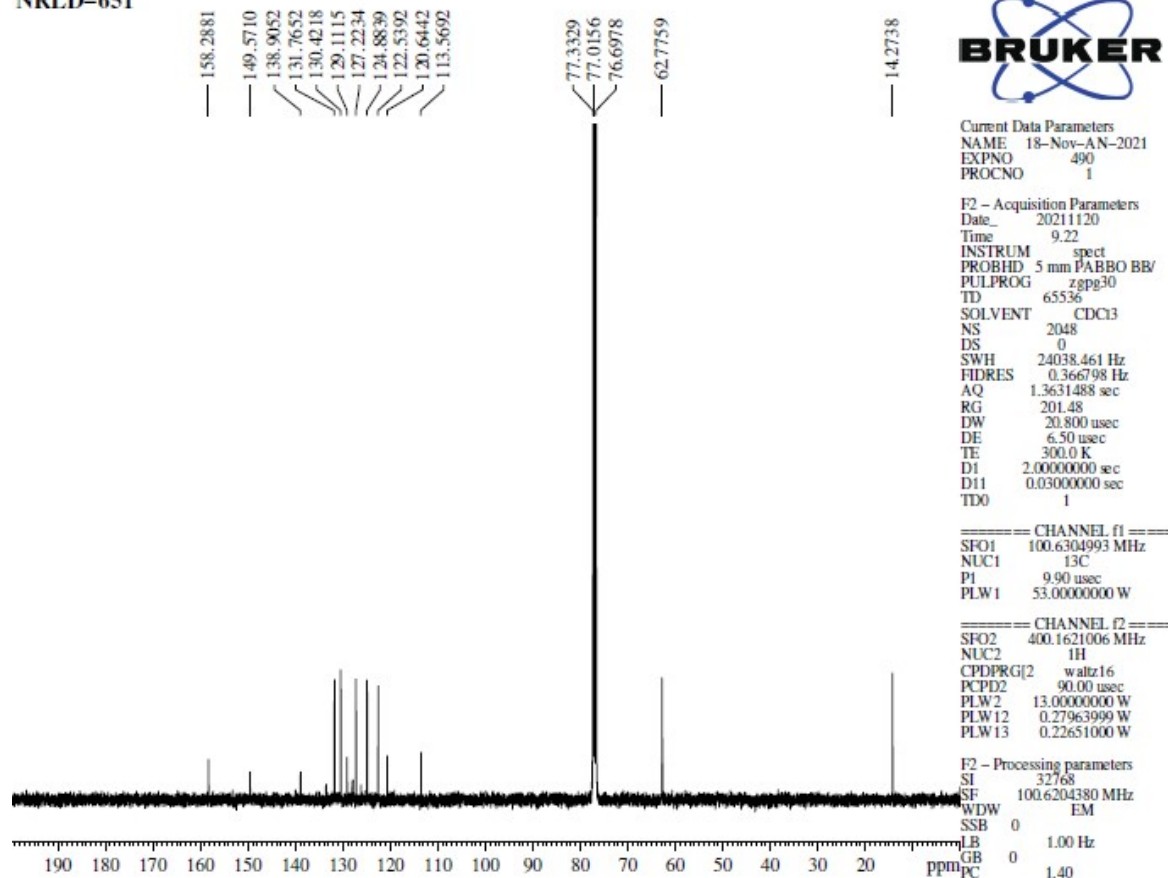


Figure S35: ¹³C NMR spectrum of 3n

NRLD 658

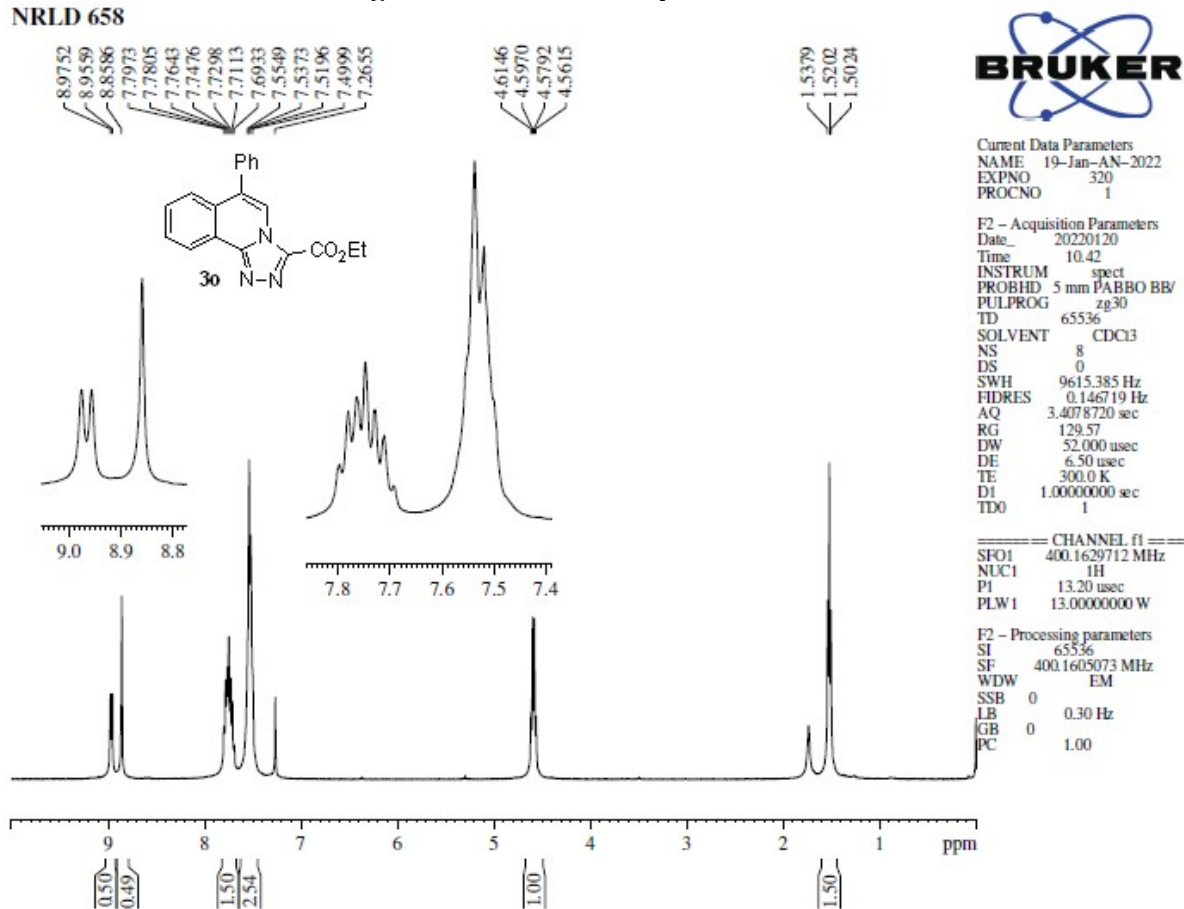


Figure S36: ¹H NMR spectrum of 3o

NRLD-658

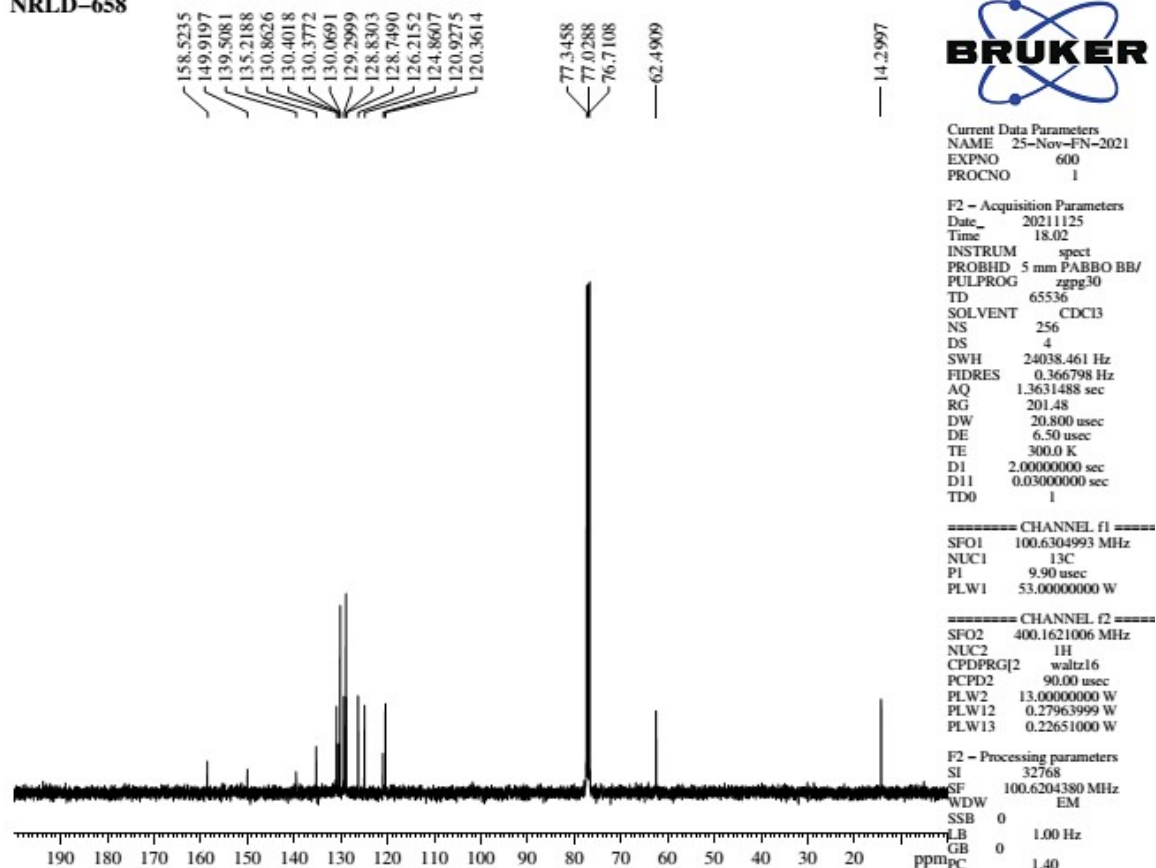


Figure S37: ¹³C NMR spectrum of 3o

NRLD-662

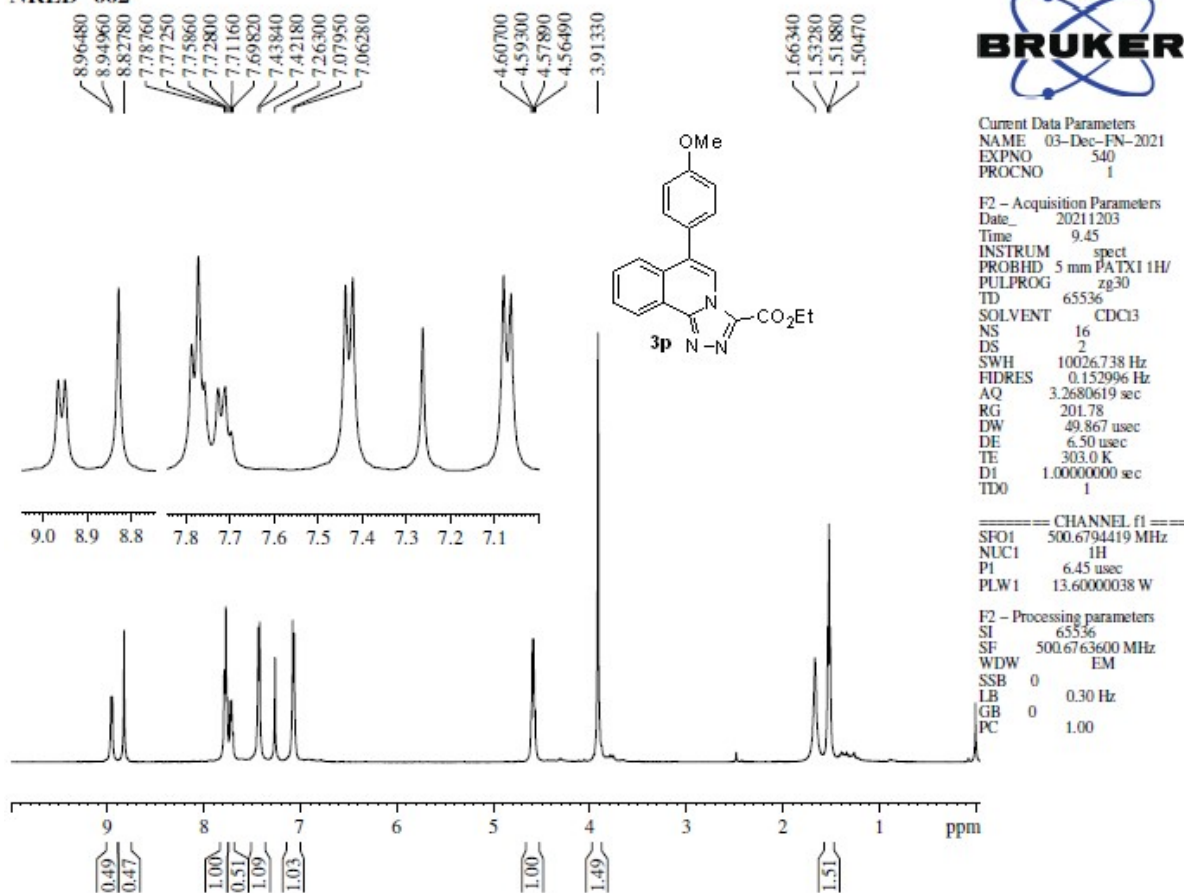


Figure S38: ¹H NMR spectrum of 3p

NRLD-662

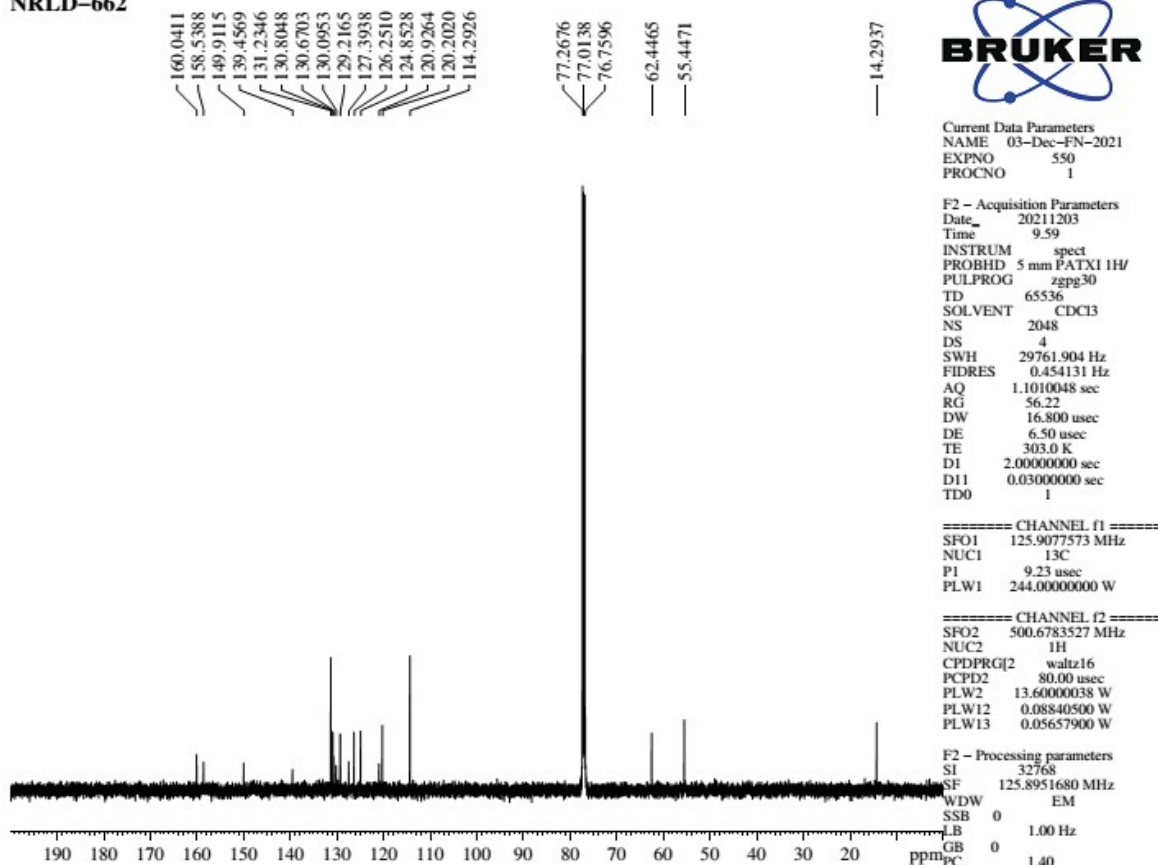


Figure S39: ¹³C NMR spectrum of 3p

NRLD-636

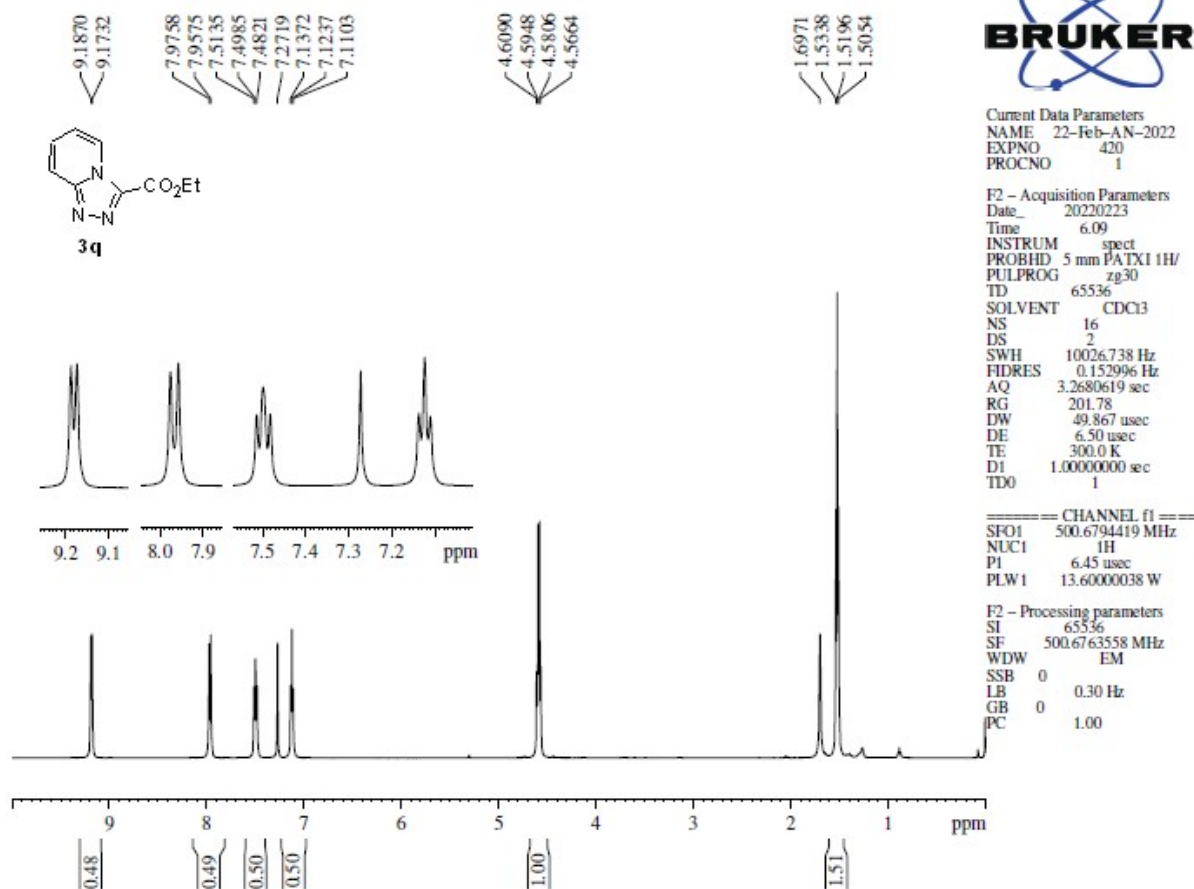


Figure S40: ¹H NMR spectrum of 3q

NRLD 636

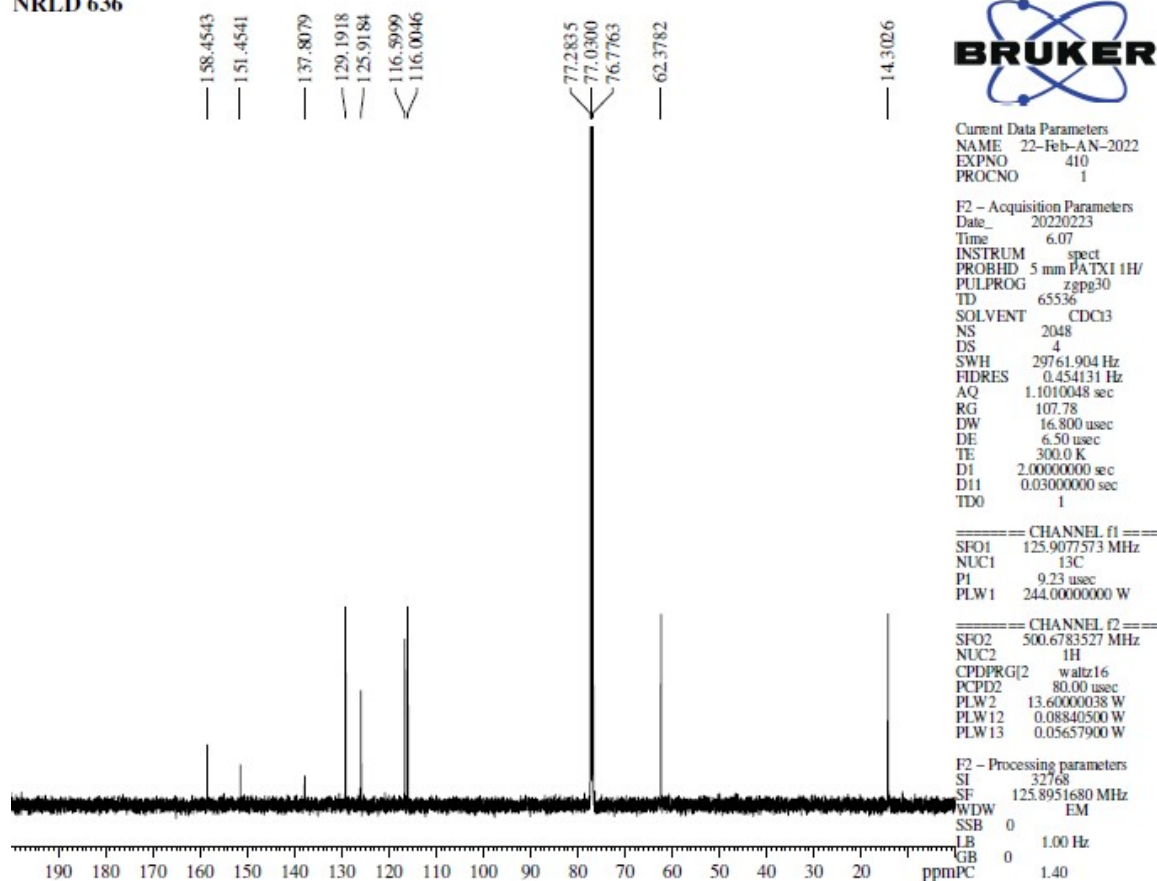


Figure S41: ¹³C NMR spectrum of 3q

NRLD-705

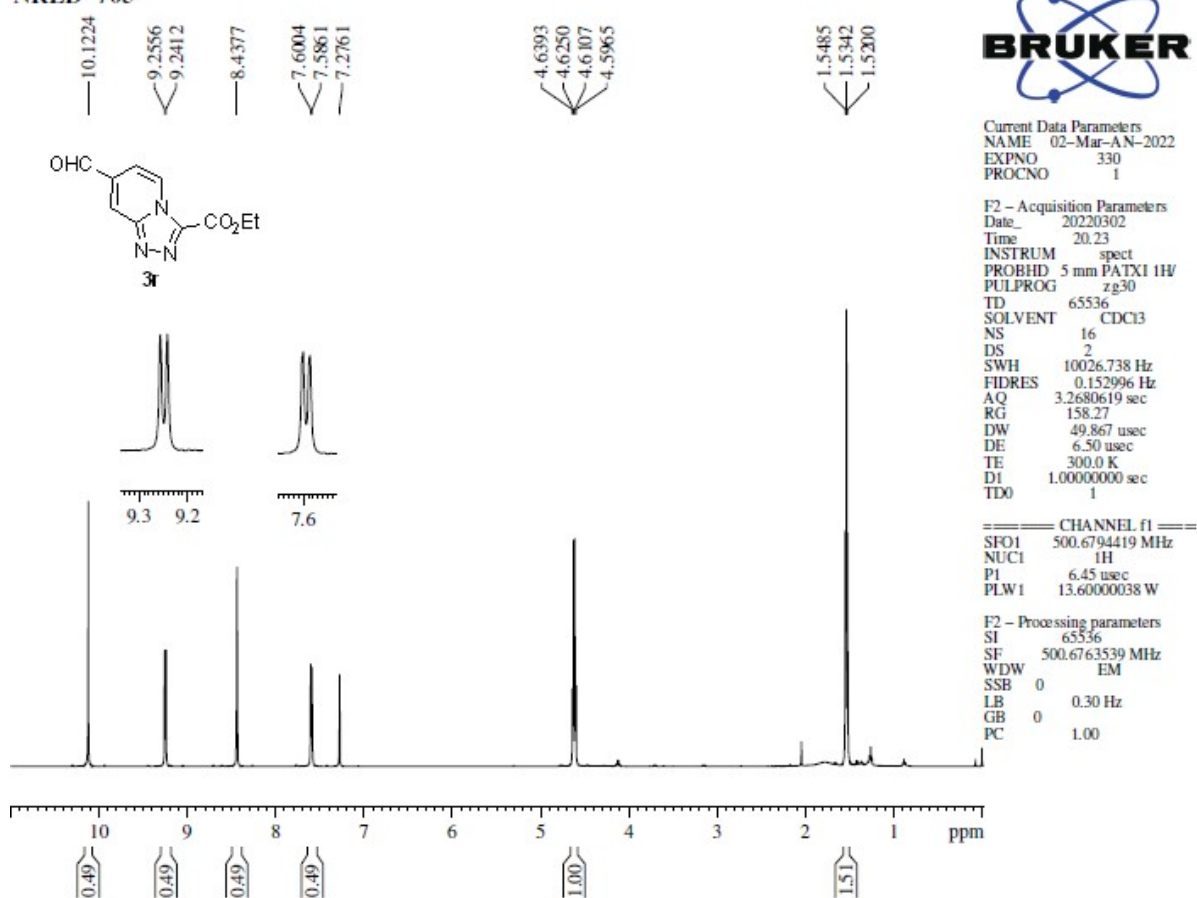
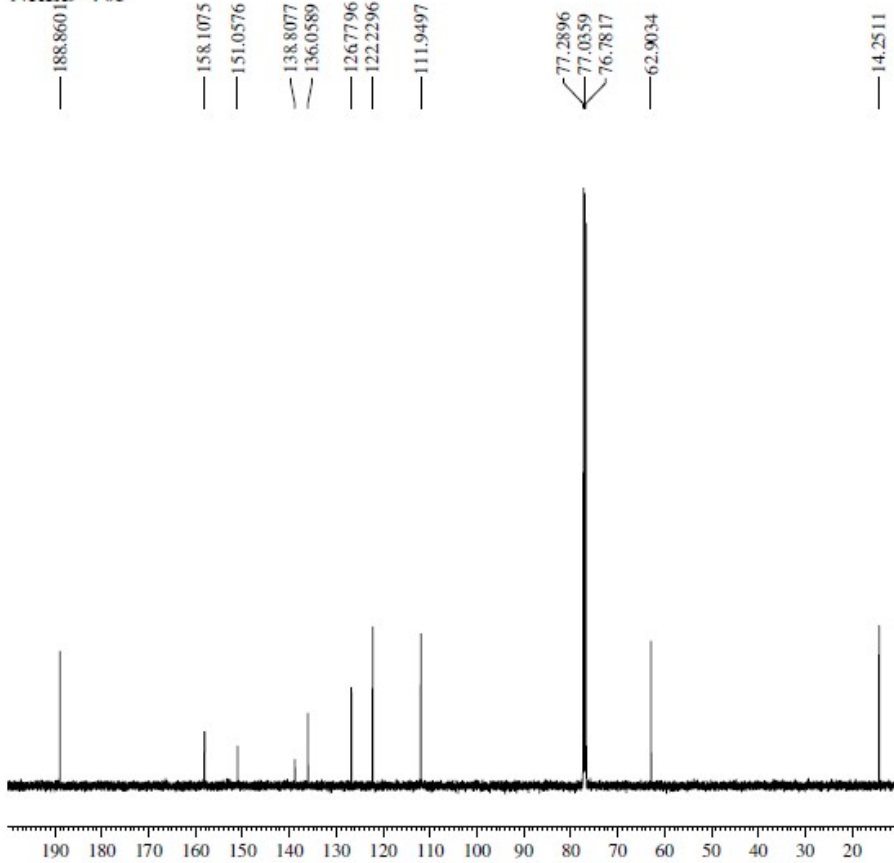


Figure S42: ¹H NMR spectrum of 3r

NRLD-705



Current Data Parameters
NAME 02-Mar-A-N-2022
EXPNO 340
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220302
Time 21.23
INSTRUM spect
PROBHD 5 mm PATXI 1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 107.78
DW 16.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

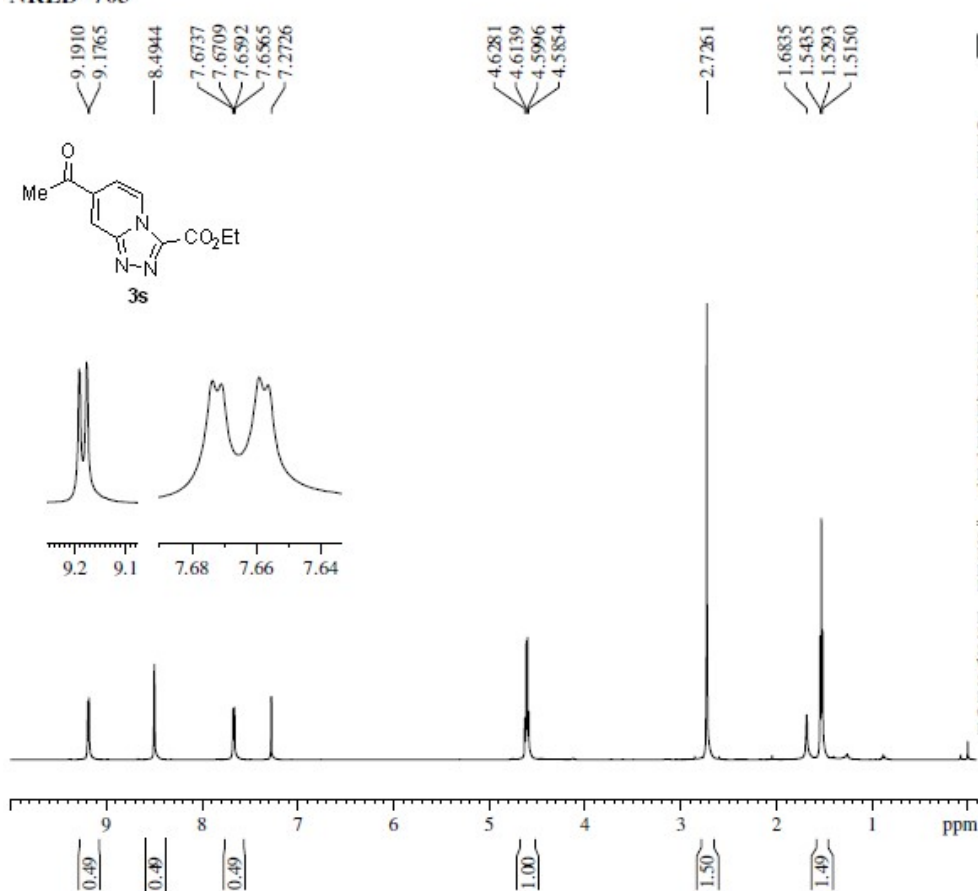
==== CHANNEL f1 ====
SFO1 125.9077573 MHz
NUC1 13C
P1 9.23 usec
PLW1 244.00000000 W

==== CHANNEL f2 ====
SFO2 500.6783527 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 80.00 usec
PLW2 13.60000038 W
PLW12 0.08840500 W
PLW13 0.05657900 W

F2 - Processing parameters
SI 32768
SF 125.8951680 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Figure S43: ¹³C NMR spectrum of 3r

NRLD-703



Current Data Parameters
NAME 02-Mar-FN-2022
EXPNO 590
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220302
Time 13.06
INSTRUM spect
PROBHD 5 mm PATXI 1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10026.738 Hz
FIDRES 0.152996 Hz
AQ 3.2680619 sec
RG 181.18
DW 49.867 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

==== CHANNEL f1 ====
SFO1 500.6794419 MHz
NUC1 1H
P1 6.45 usec
PLW1 13.60000038 W

F2 - Processing parameters
SI 65536
SF 500.6763556 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Figure S44: ¹H NMR spectrum of 3s

NRLD-703

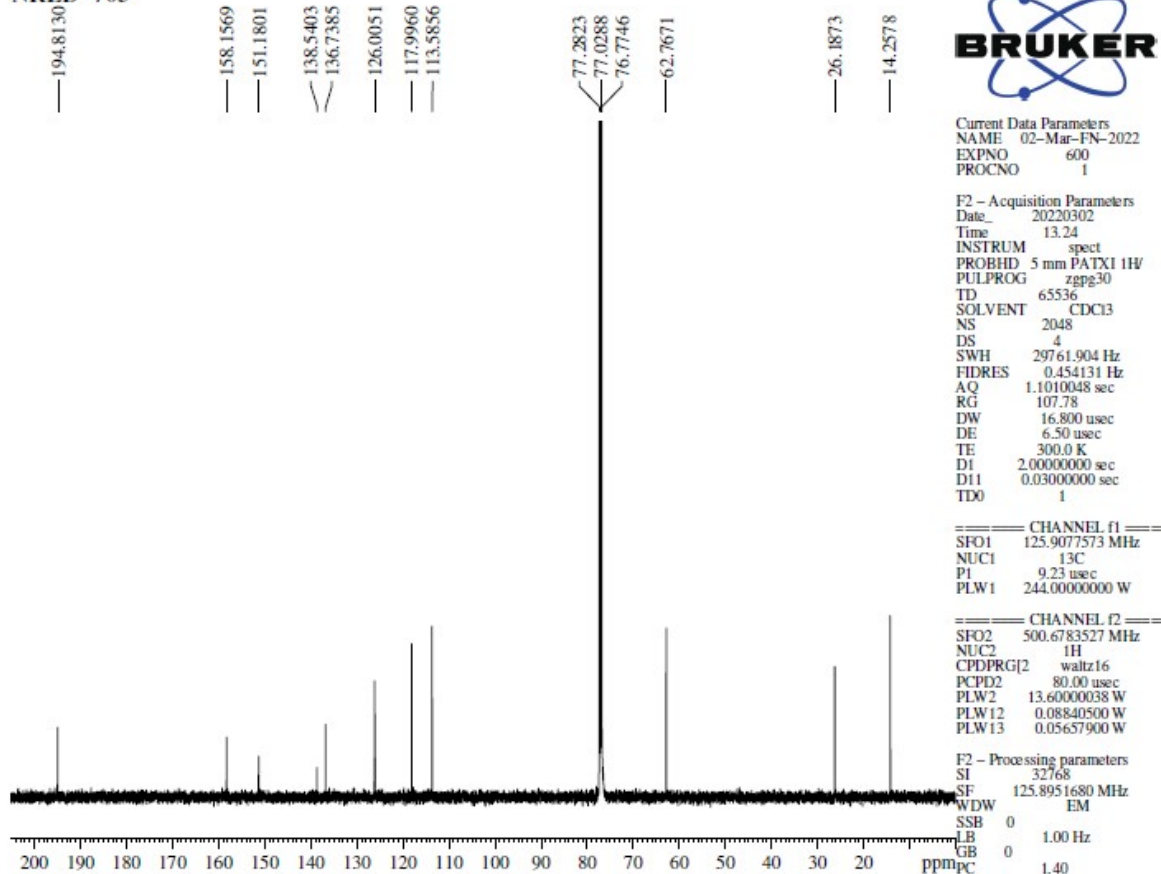


Figure S45: ¹³C NMR spectrum of 3s

NRLD-707

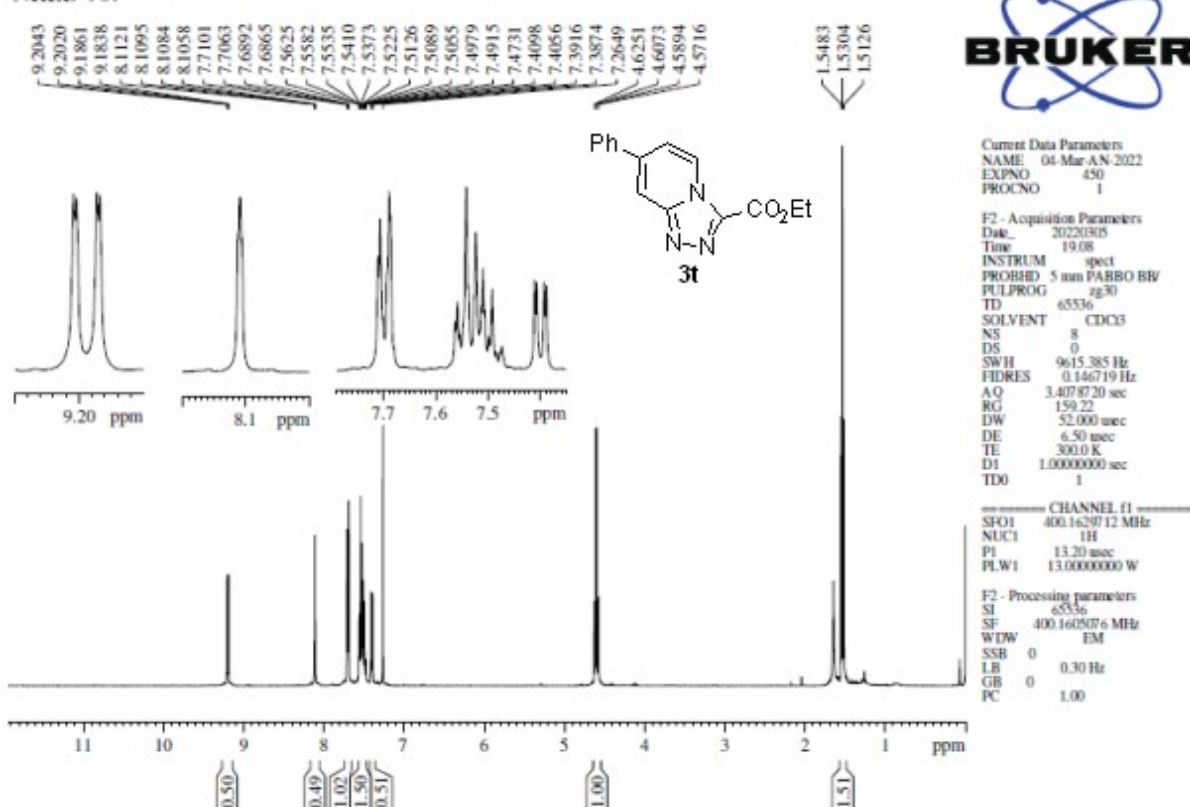


Figure S46: ¹H NMR spectrum of 3t

NRLD-707

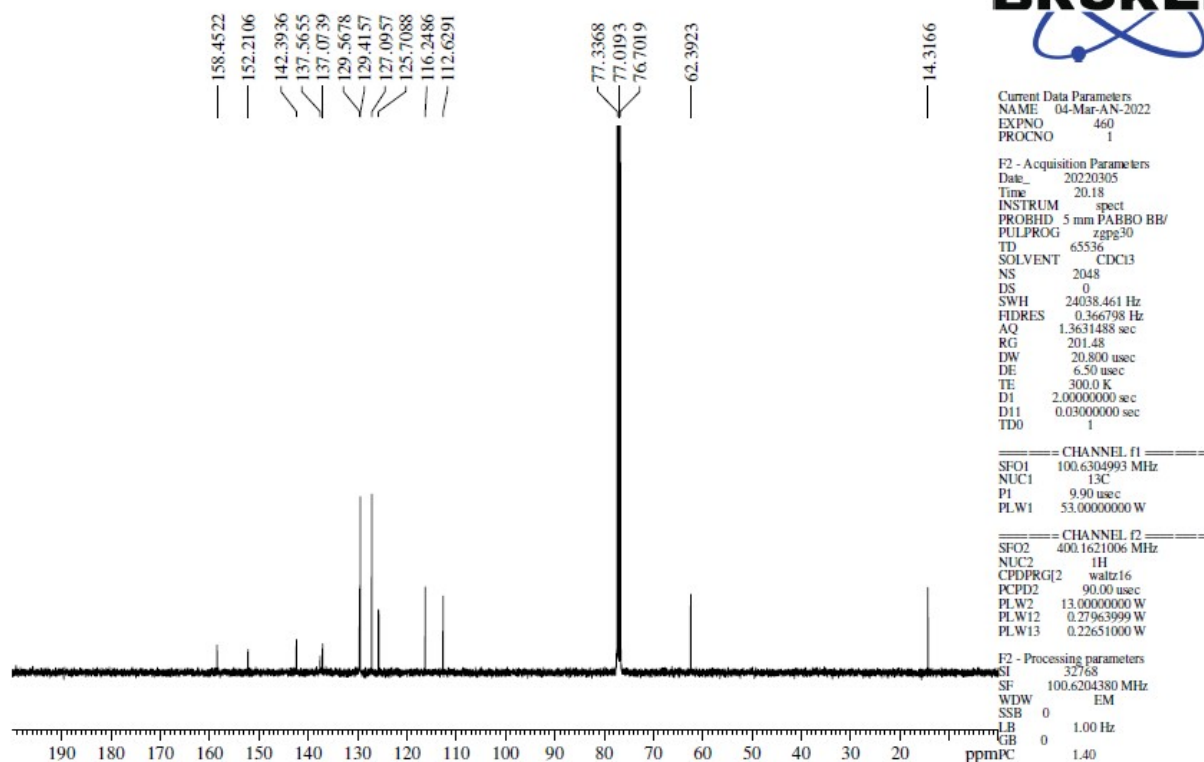


Figure S47: ¹³C NMR spectrum of 3t

NRLD 724

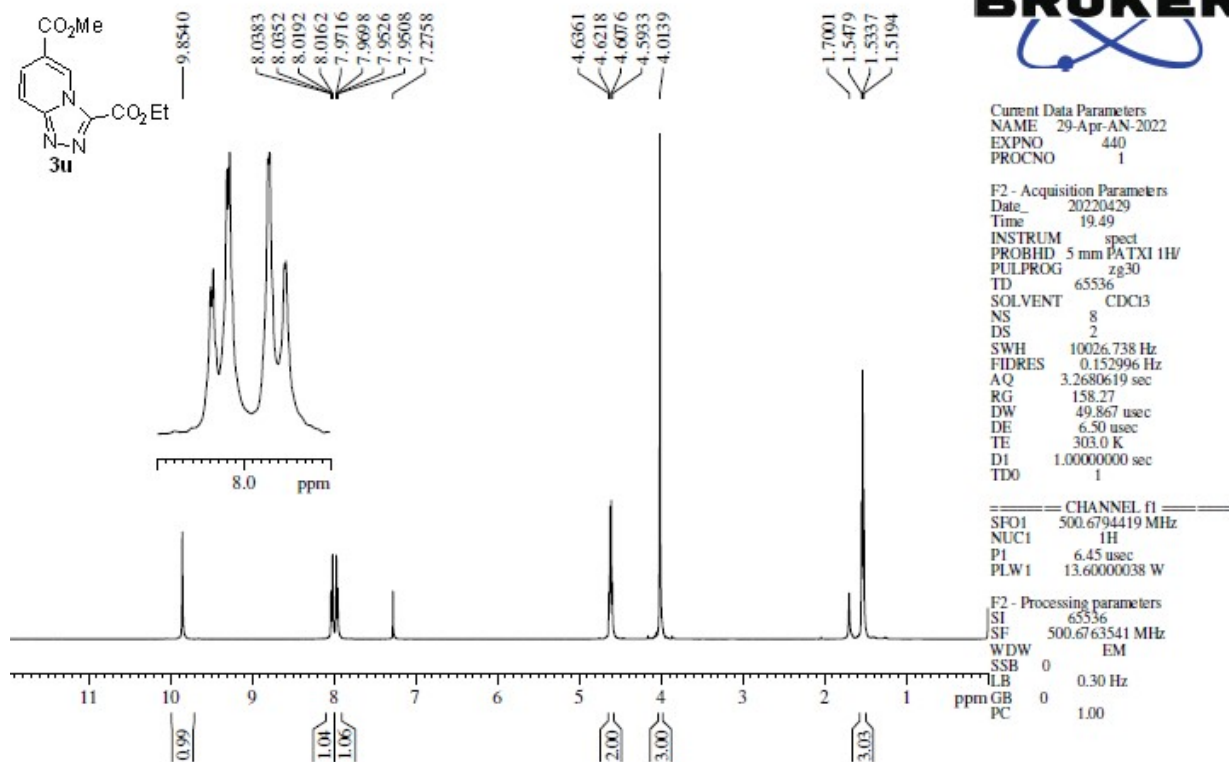


Figure S48: ¹H NMR spectrum of 3u

NRLD 724

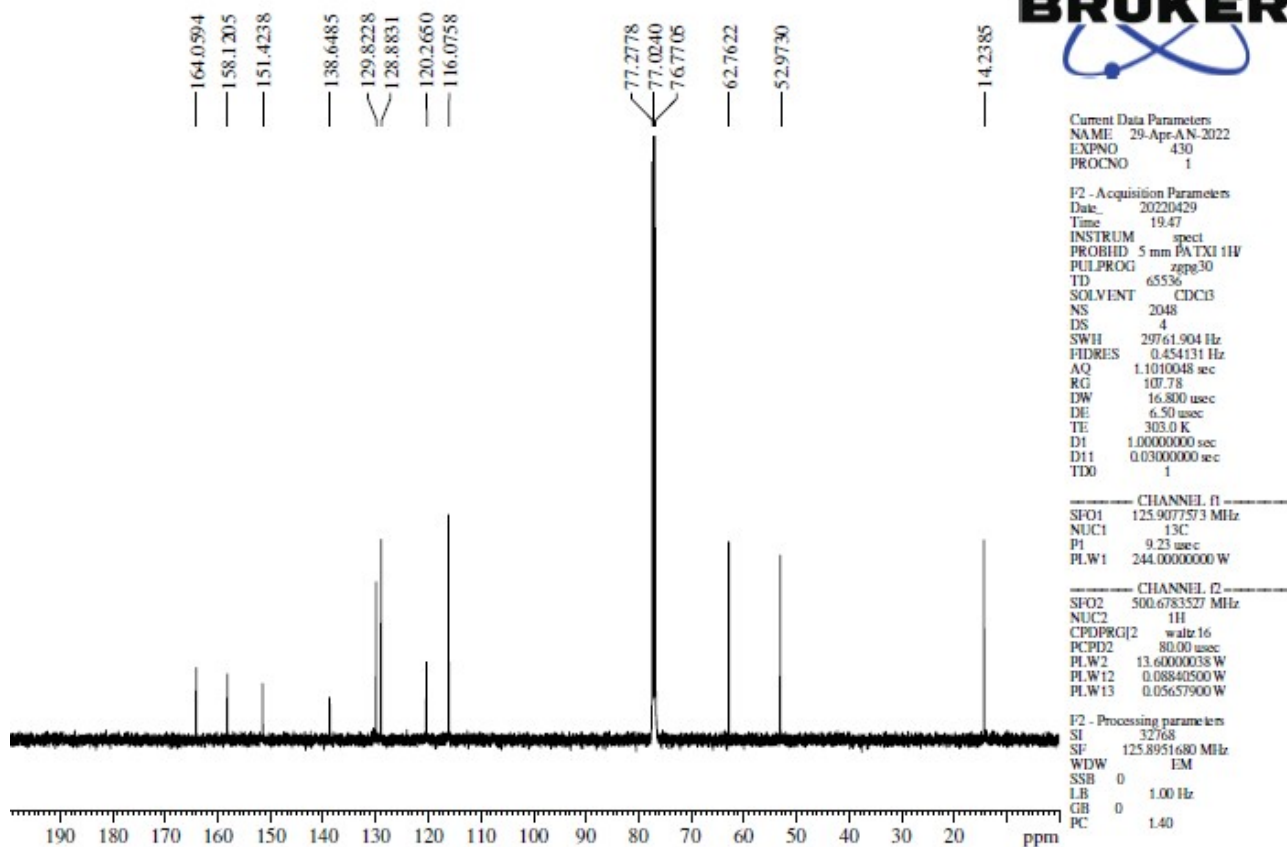


Figure S49: ¹³C NMR spectrum of 3u

NRLD-725

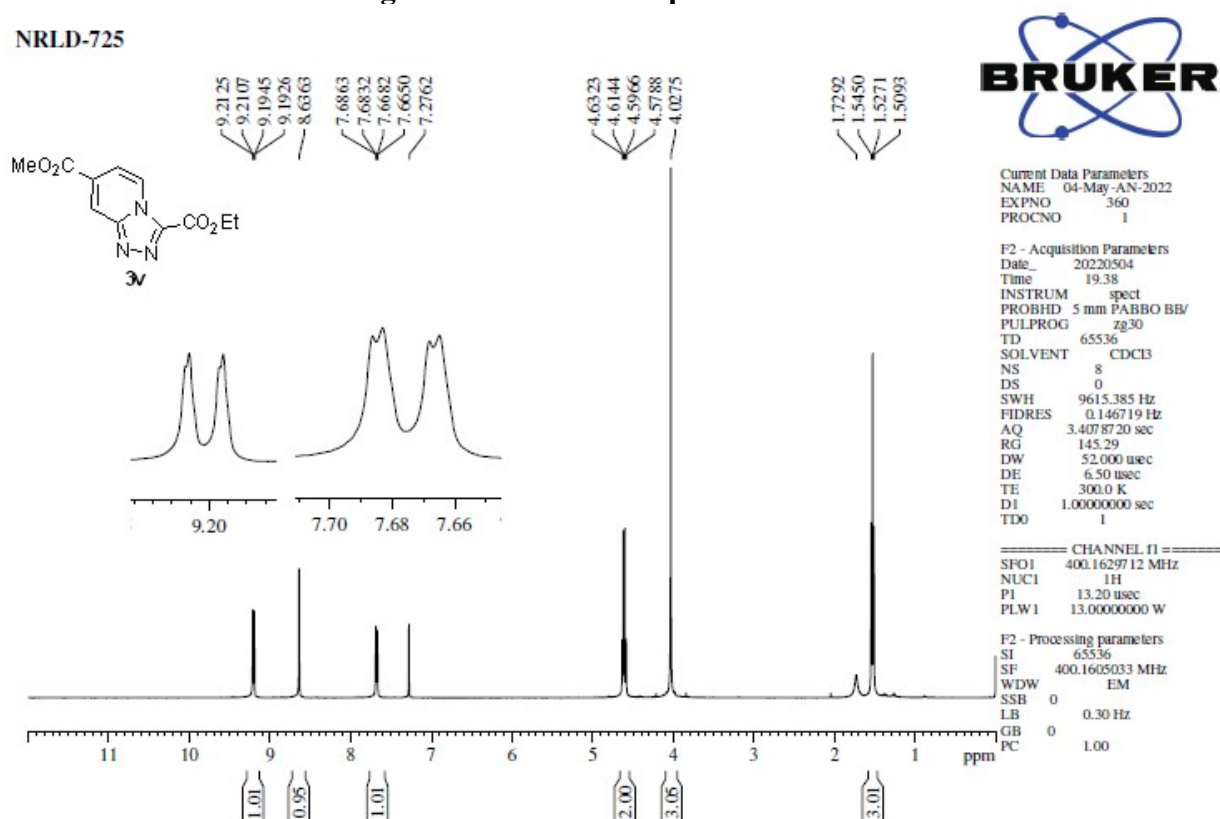
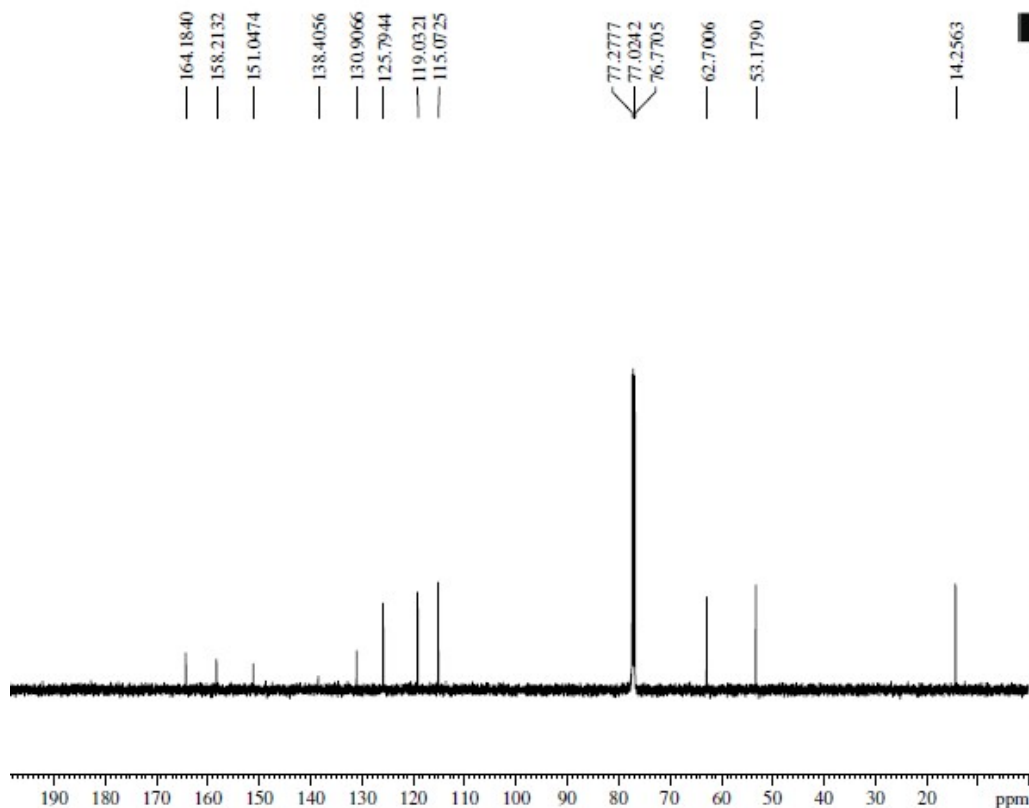


Figure S50: ¹H NMR spectrum of 3v

NRLD 725



Current Data Parameters
 NAME 02-May-AN-2022
 EXPNO 350
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20220503
 Time 0.42
 INSTRUM spect
 PROBHD 5 mm PATXI 1H/1
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 2048
 DS 4
 SWH 29761.904 Hz
 FIDRES 0.454131 Hz
 AQ 1.1010048 sec
 RG 56.22
 DW 16.800 usec
 DE 6.50 usec
 TE 303.0 K
 D1 1.00000000 sec
 D11 0.03000000 sec
 TDO 1

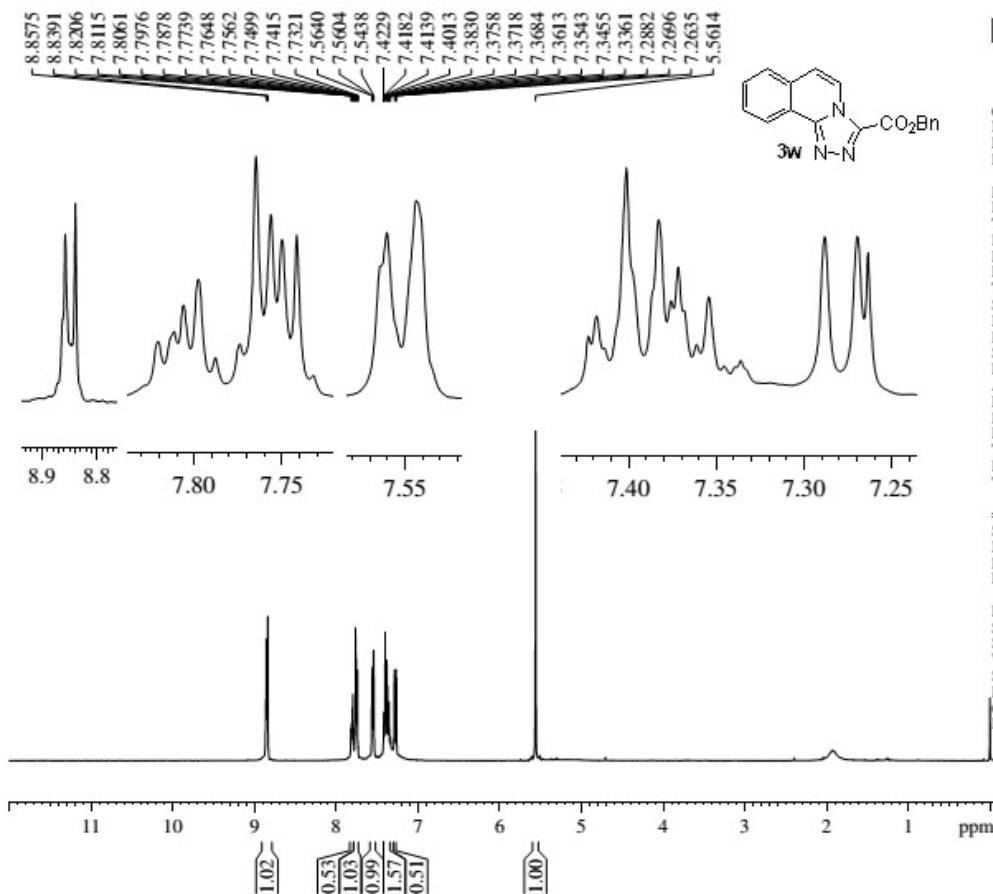
==== CHANNEL f1 =====
 SFO1 125.9077573 MHz
 NUC1 13C
 P1 9.23 usec
 PLW1 244.00000000 W

==== CHANNEL f2 =====
 SFO2 500.6783527 MHz
 NUC2 1H
 CPDPRG2 waltz 16
 PCPD2 80.00 usec
 PLW2 13.60000038 W
 PLW12 0.08840500 W
 PLW13 0.05657900 W

F2 - Processing parameters
 SI 32768
 SF 125.8951680 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

Figure S51: ¹³C NMR spectrum of 3v

NRLD-641



Current Data Parameters
 NAME 23-Nov-AN-2021
 EXPNO 490
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20211124
 Time 4.47
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 8
 DS 0
 SWH 9615.385 Hz
 FIDRES 0.146719 Hz
 AQ 3.4078720 sec
 RG 129.57
 DW 52.000 usec
 DE 6.50 usec
 TE 300.0 K
 D1 1.00000000 sec
 TDO 1

==== CHANNEL f1 =====
 SFO1 400.1629712 MHz
 NUC1 1H
 P1 13.20 usec
 PLW1 13.00000000 W

F2 - Processing parameters
 SI 65536
 SF 400.1605082 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

Figure S52: ¹H NMR spectrum of 3w

NRLD-641

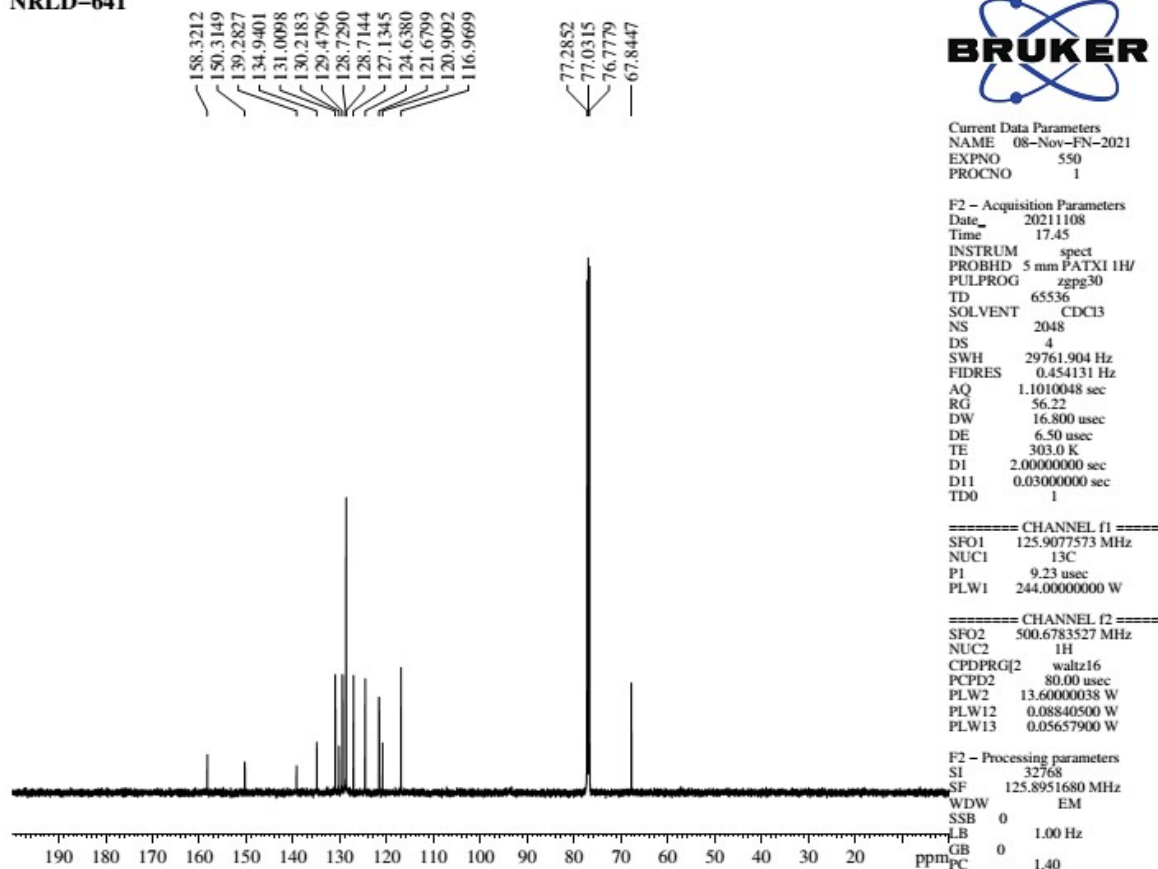


Figure S53: ¹³C NMR spectrum of 3w

NRLD-654

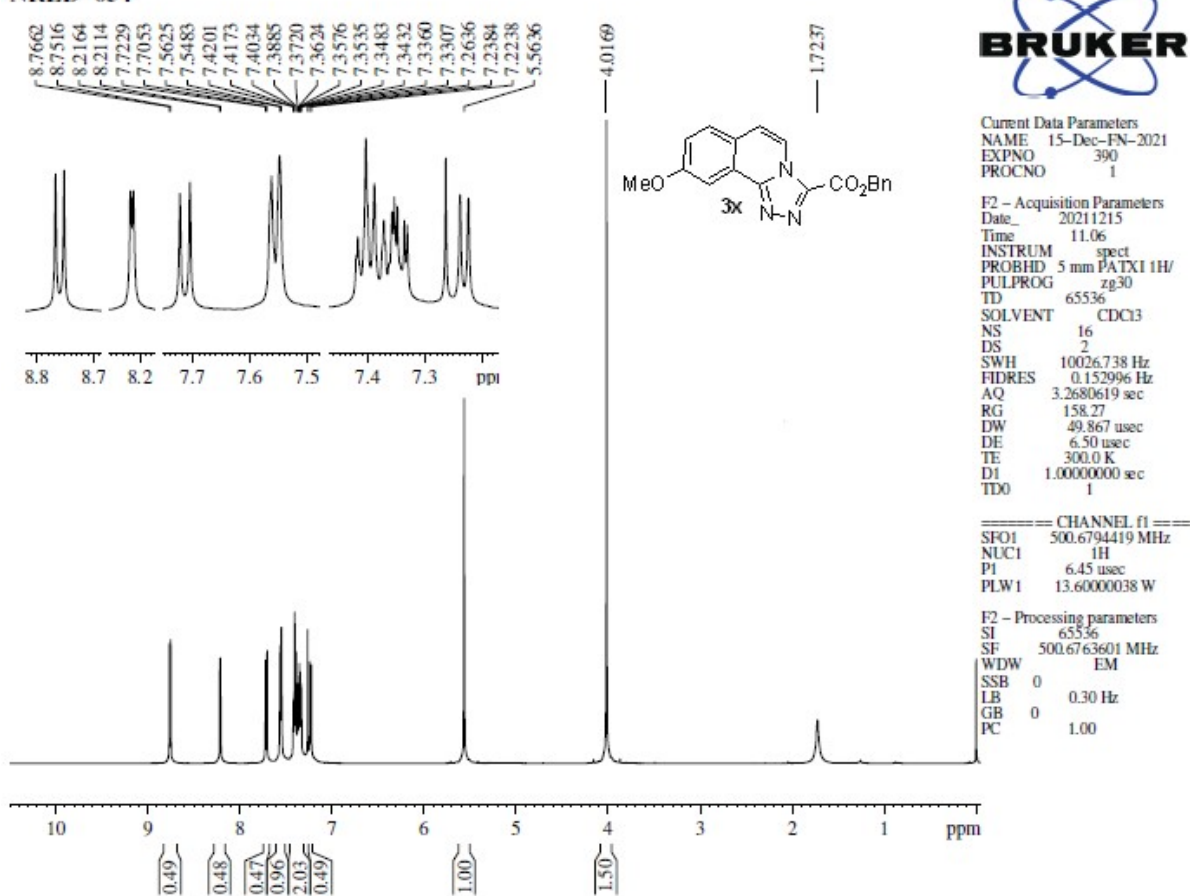


Figure S54: ¹H NMR spectrum of 3x

NRLD-654

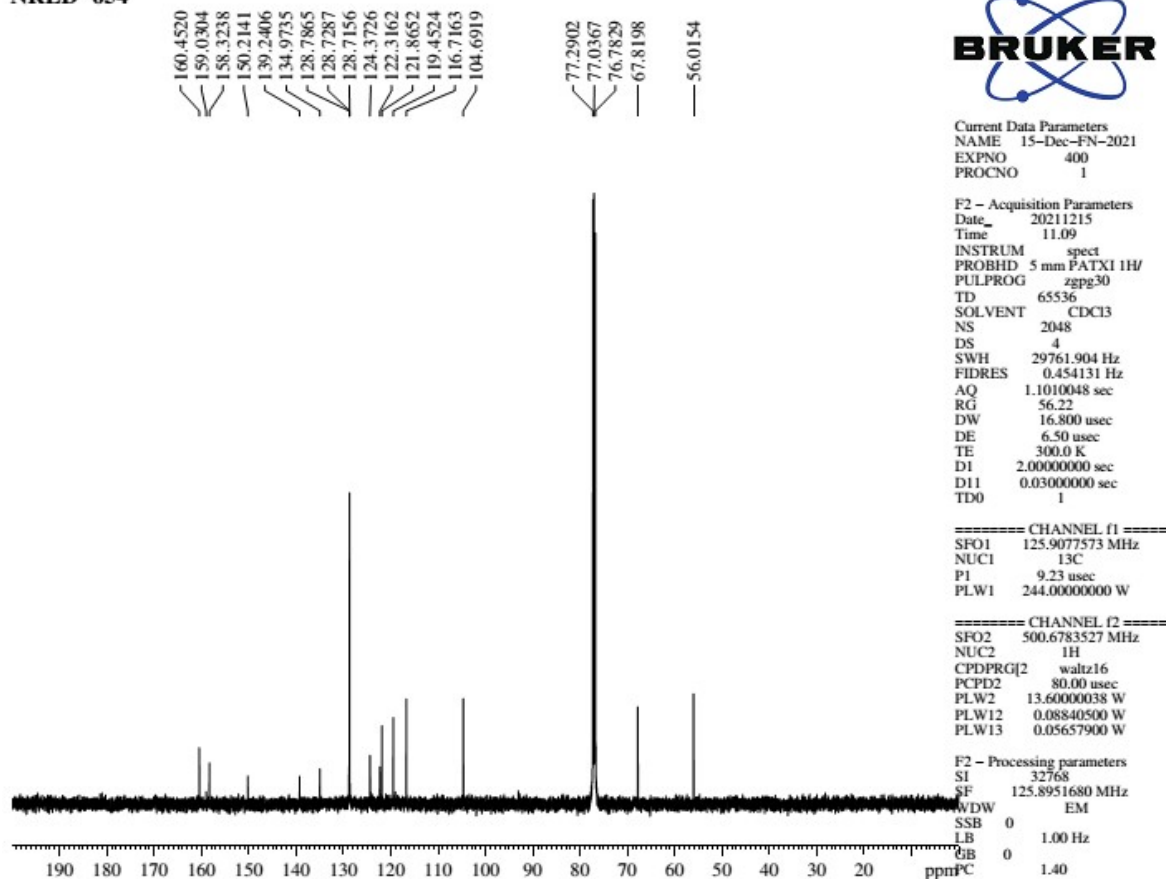


Figure S55: ¹³C NMR spectrum of 3x

NRLD-642

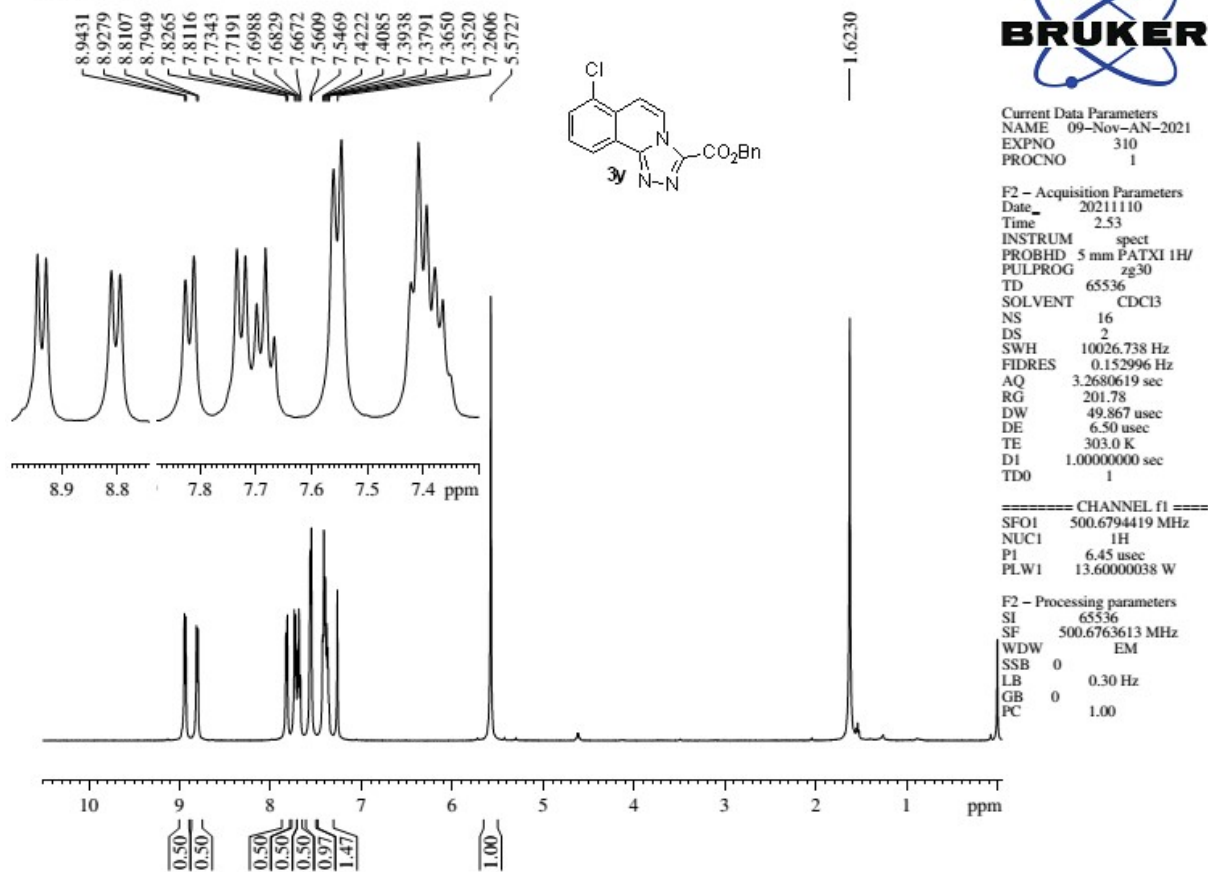


Figure S56: ¹H NMR spectrum of 3y

NRLD-642

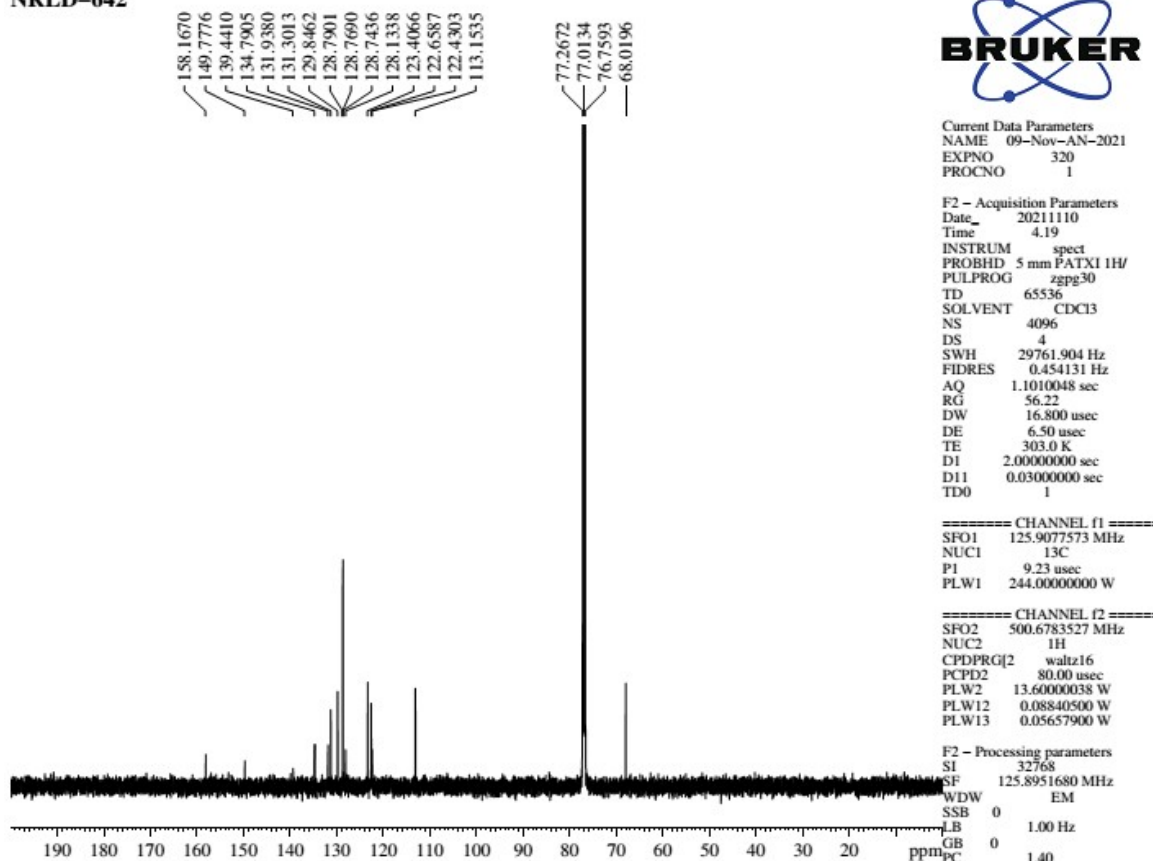


Figure S57: ¹³C NMR spectrum of 3y

NRLD-688

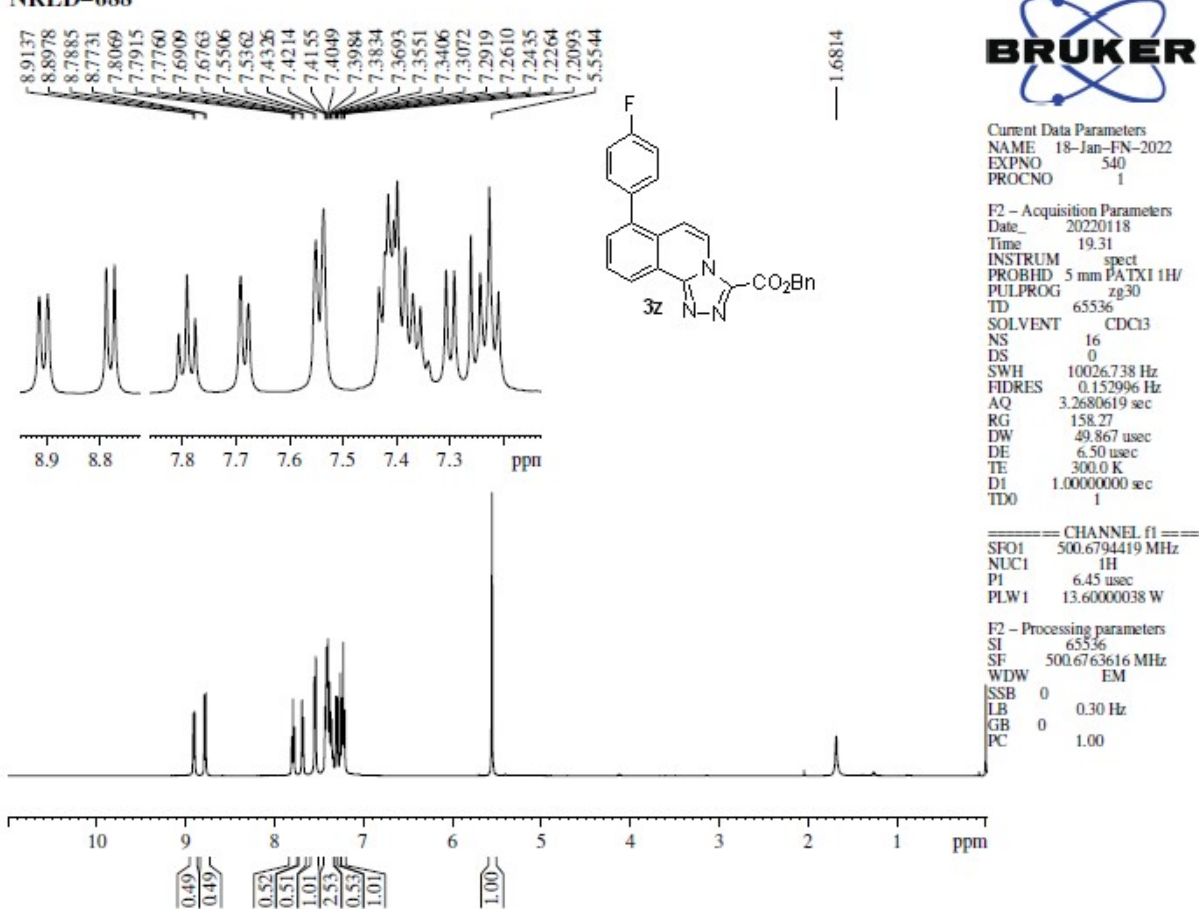
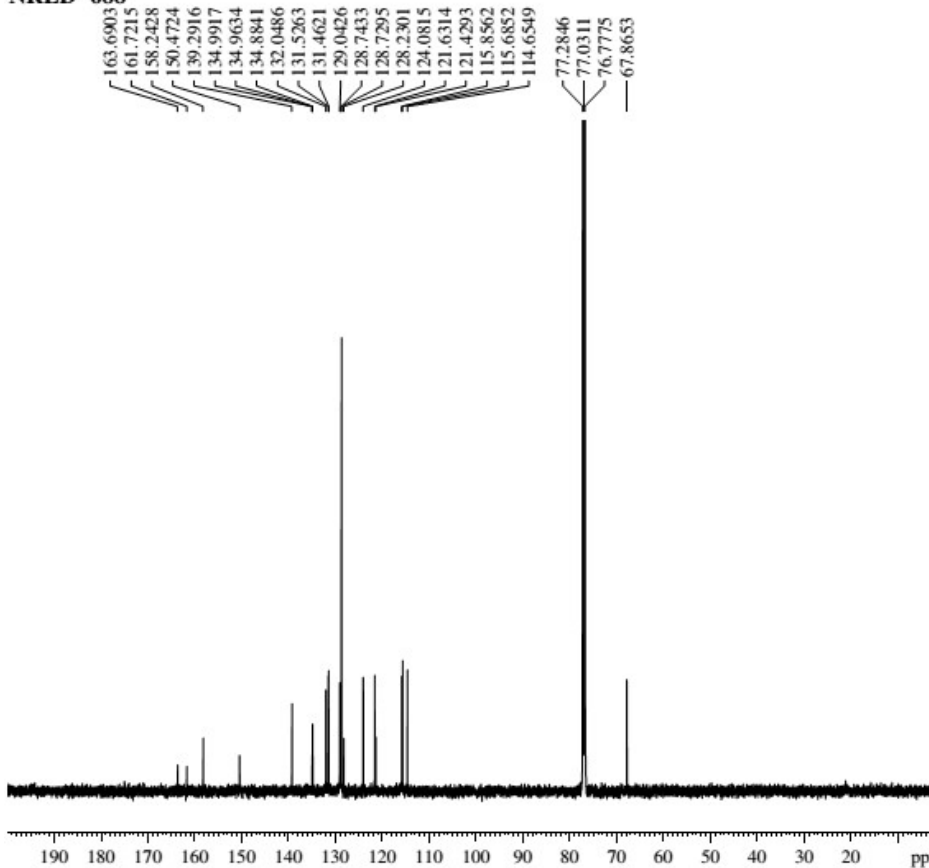


Figure S58: ¹H NMR spectrum of 3z

NRLD-688



Current Data Parameters
 NAME 18-Jan-FN-2022
 EXPNO 550
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20220118
 Time 21.21
 INSTRUM spect
 PROBHD 5 mm FATXI 1H/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 2048
 DS 0
 SWH 29761.904 Hz
 FIDRES 0.454131 Hz
 AQ 1.1010048 sec
 RG 87.95
 DW 16.800 usec
 DE 6.50 usec
 TE 300.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

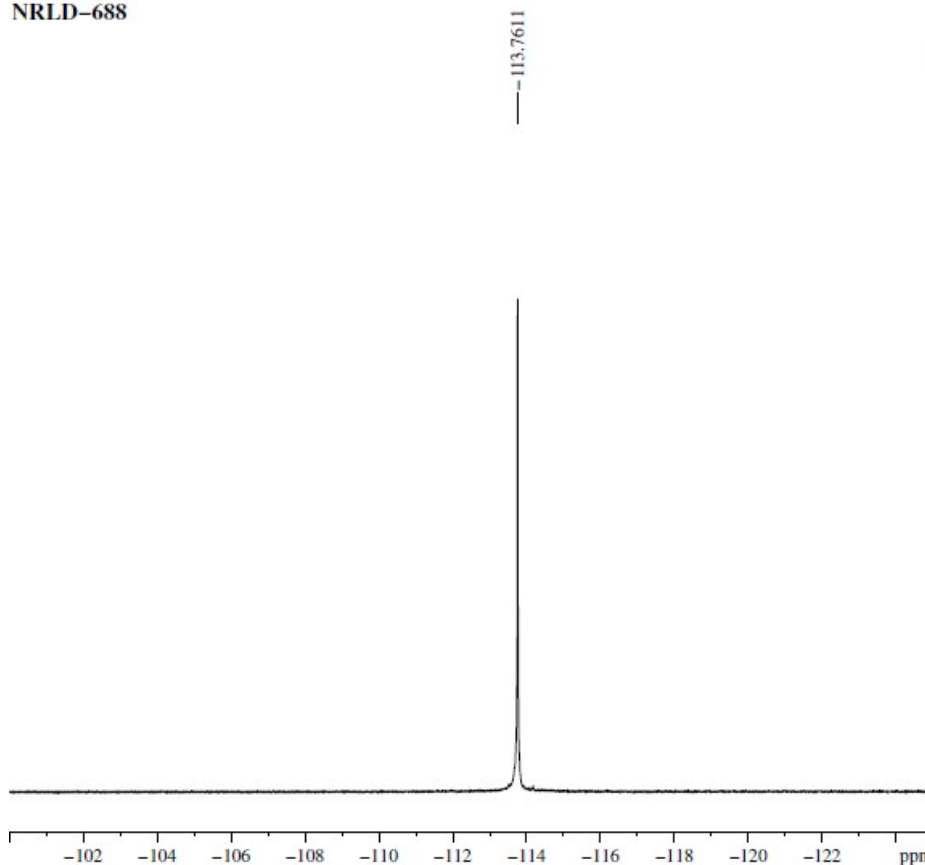
==== CHANNEL f1 ====
 SFO1 125.9077573 MHz
 NUC1 13C
 P1 9.23 usec
 PLW1 244.00000000 W

==== CHANNEL f2 ====
 SFO2 500.6783527 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 80.00 usec
 PLW2 13.60000038 W
 PLW12 0.08840500 W
 PLW13 0.05657900 W

F2 - Processing parameters
 SI 32768
 SF 125.8951680 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

Figure S59: ¹³C NMR spectrum of 3z

NRLD-688



Current Data Parameters
 NAME 20-Jan-FN-2022
 EXPNO 580
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20220121
 Time 3.57
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgfhgqn.2
 TD 131072
 SOLVENT CDCl3
 NS 16
 DS 4
 SWH 89285.711 Hz
 FIDRES 0.681196 Hz
 AQ 0.7340032 sec
 RG 201.48
 DW 5.600 usec
 DE 6.50 usec
 TE 300.0 K
 D1 1.00000000 sec
 D11 0.03000000 sec
 D12 0.00002000 sec
 TD0 1

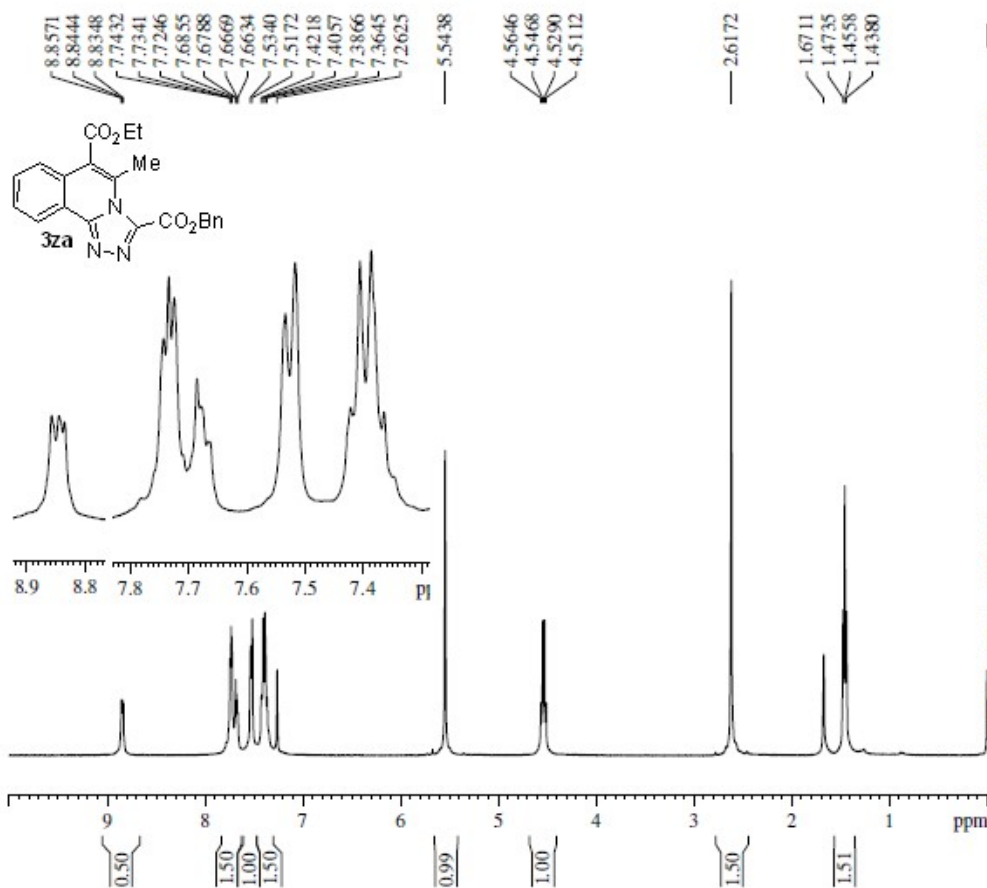
==== CHANNEL f1 ====
 SFO1 376.4894122 MHz
 NUC1 19F
 P1 15.00 usec
 PLW1 21.00000000 W

==== CHANNEL f2 ====
 SFO2 400.1621006 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 90.00 usec
 PLW2 13.00000000 W
 PLW12 0.27963999 W

F2 - Processing parameters
 SI 65536
 SF 376.5270650 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

Figure S60: ¹⁹F NMR spectrum of 3z

NRLD-666



Current Data Parameters
 NAME 13-Jan-AN-2022
 EXPNO 40
 PROCNO 1

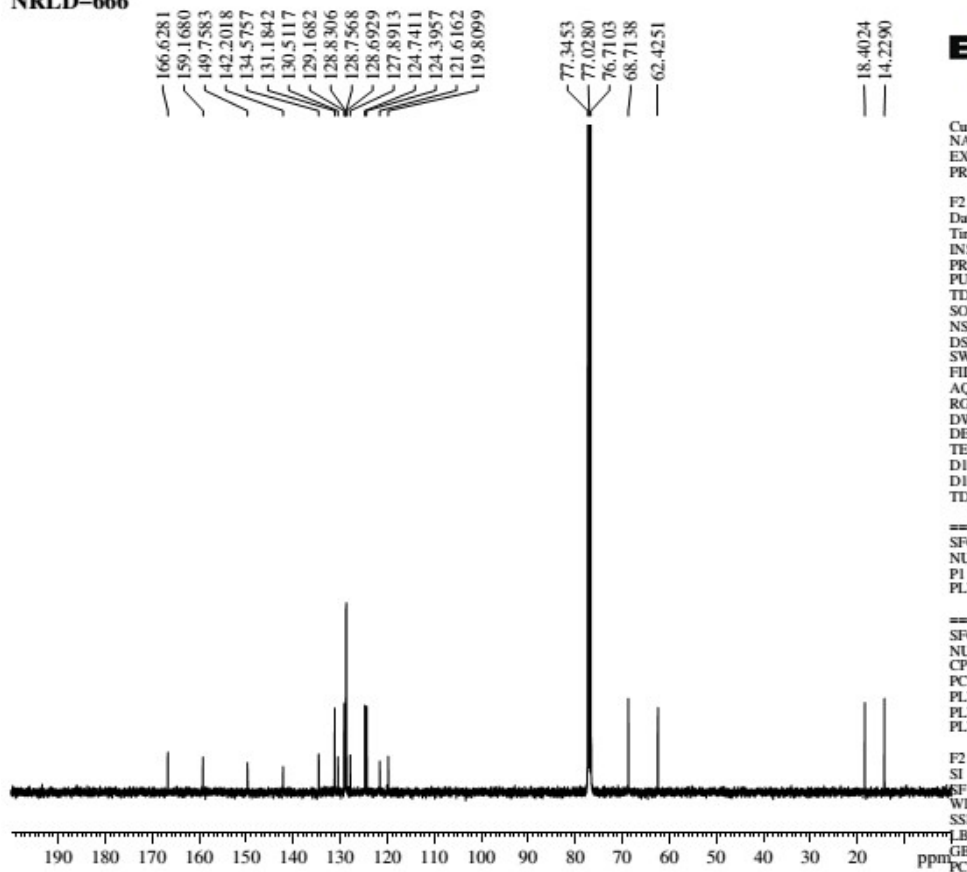
F2 - Acquisition Parameters
 Date_ 20220113
 Time 20.42
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 8
 DS 0
 SWH 9615.385 Hz
 FIDRES 0.146719 Hz
 AQ 3.4078720 sec
 RG 129.57
 DW 52.000 usec
 DE 6.50 usec
 TE 300.0 K
 D1 1.00000000 sec
 TD0 1

==== CHANNEL f1 ====
 SFO1 400.1629712 MHz
 NUC1 1H
 P1 13.20 usec
 PLW1 13.00000000 W

F2 - Processing parameters
 SI 65536
 SF 400.1605081 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

Figure S61: ¹H NMR spectrum of 3za

NRLD-666



Current Data Parameters
 NAME 13-Jan-AN-2022
 EXPNO 450
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20220113
 Time 21.29
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 2048
 DS 0
 SWH 24038.461 Hz
 FIDRES 0.366798 Hz
 AQ 1.3631488 sec
 RG 201.48
 DW 20.800 usec
 DE 6.50 usec
 TE 300.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

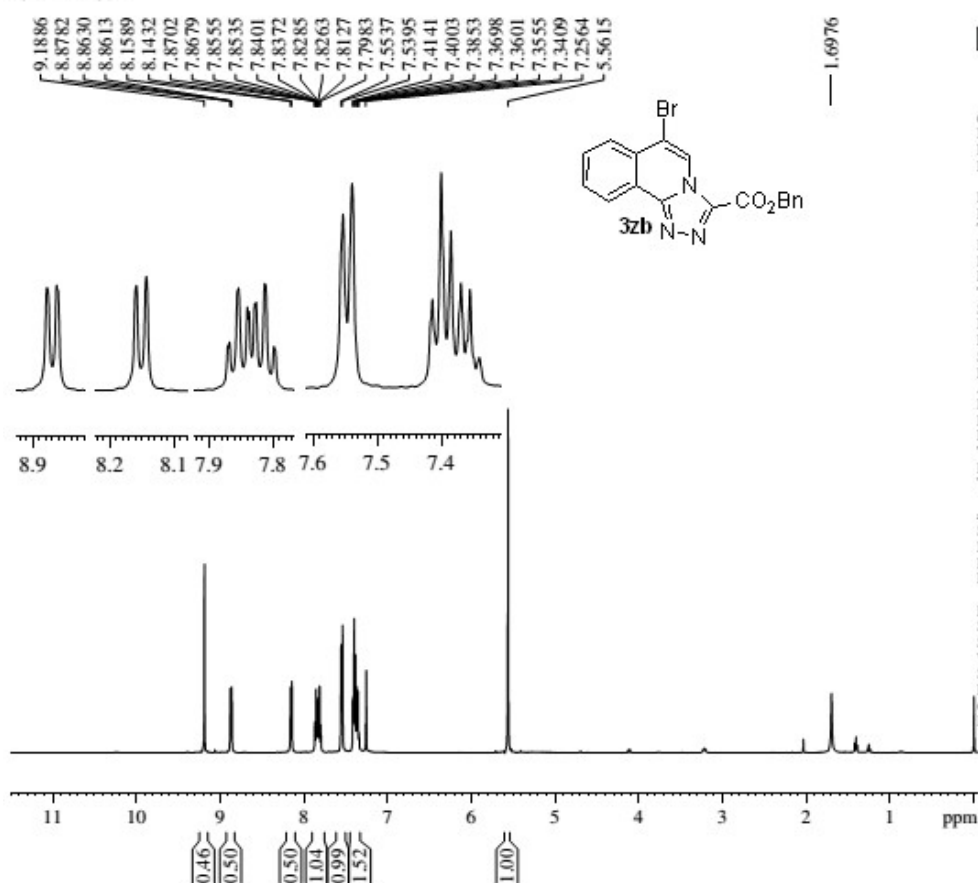
==== CHANNEL f1 ====
 SFO1 100.6304993 MHz
 NUC1 13C
 P1 9.90 usec
 PLW1 53.00000000 W

==== CHANNEL f2 ====
 SFO2 400.1621006 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 90.00 usec
 PLW2 13.00000000 W
 PLW12 0.27963999 W
 PLW13 0.22651000 W

F2 - Processing parameters
 SI 32768
 SF 100.6204380 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

Figure S62: ¹³C NMR spectrum of 3za

NRLD-652



Current Data Parameters
 NAME 17-Nov-FN-2021
 EXPNO 460
 PROCNO 1

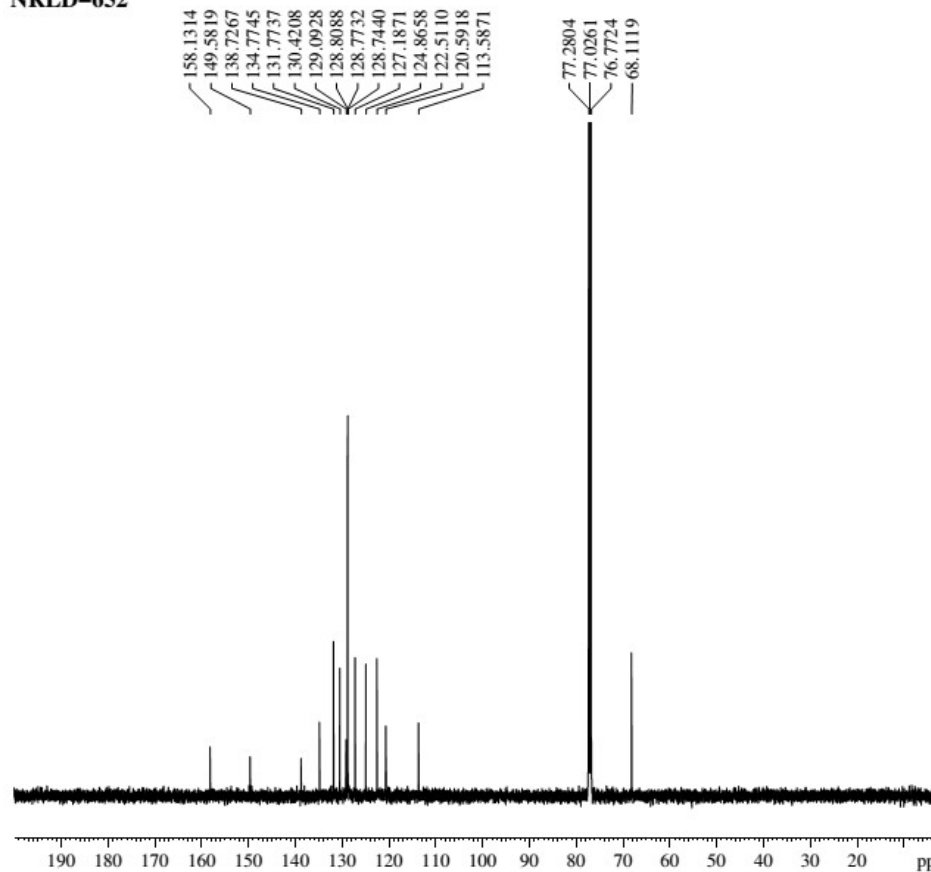
F2 - Acquisition Parameters
 Date_ 20211117
 Time 15.04
 INSTRUM spect
 PROBHD 5 mm PATXI 1H/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 10026.738 Hz
 FIDRES 0.152996 Hz
 AQ 3.2680619 sec
 RG 158.27
 DW 49.867 usec
 DE 6.50 usec
 TE 303.0 K
 D1 1.0000000 sec
 TD0 1

===== CHANNEL f1 =====
 SFO1 500.6794419 MHz
 NUC1 1H
 P1 6.45 usec
 PLW1 13.6000038 W

F2 - Processing parameters
 SI 65536
 SF 500.6763635 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

Figure S63: ¹H NMR spectrum of 3zb

NRLD-652



Current Data Parameters
 NAME 17-Nov-FN-2021
 EXPNO 470
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20211117
 Time 15.58
 INSTRUM spect
 PROBHD 5 mm PATXI 1H/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 2048
 DS 4
 SWH 29761.904 Hz
 FIDRES 0.454131 Hz
 AQ 1.1010048 sec
 RG 56.22
 DW 16.800 usec
 DE 6.50 usec
 TE 303.0 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TD0 1

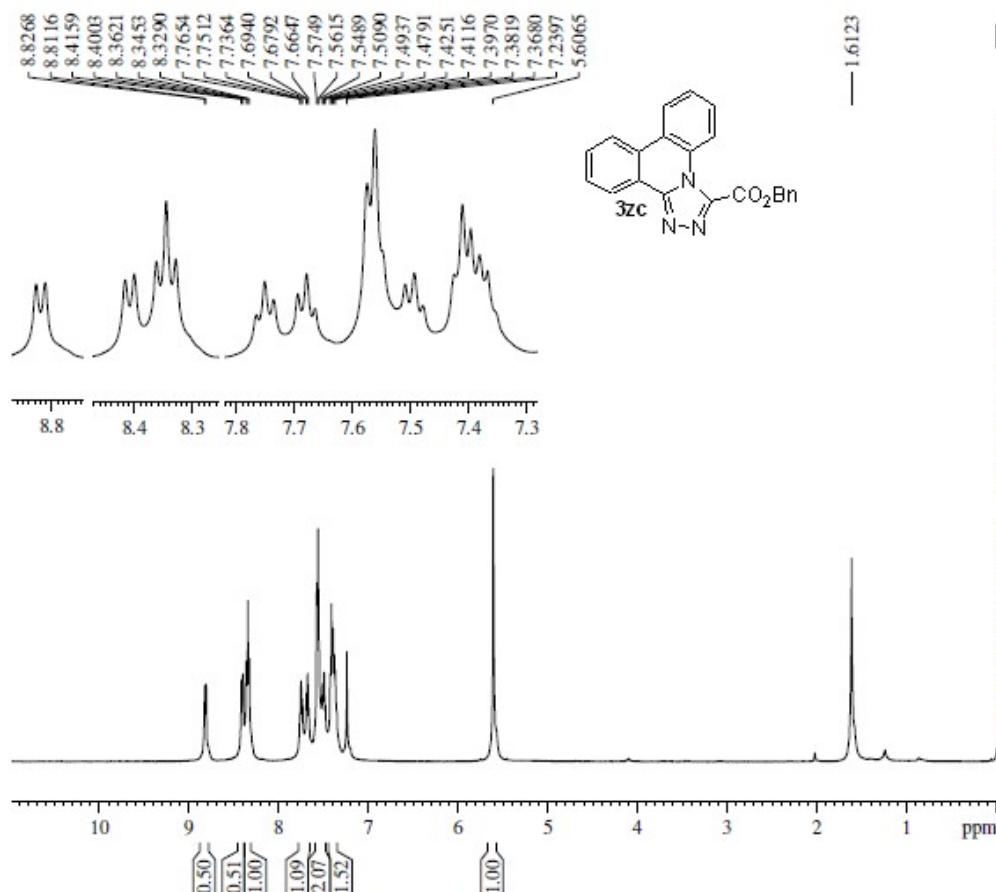
===== CHANNEL f1 =====
 SFO1 125.9077573 MHz
 NUC1 13C
 P1 9.23 usec
 PLW1 244.0000000 W

===== CHANNEL f2 =====
 SFO2 500.6783527 MHz
 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 80.00 usec
 PLW2 13.6000038 W
 PLW12 0.08840500 W
 PLW13 0.05657900 W

F2 - Processing parameters
 SI 32768
 SF 125.8951680 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

Figure S64: ¹³C NMR spectrum of 3zb

NRLD-659



Current Data Parameters
 NAME 07-Dec-FN-2021
 EXPNO 570
 PROCNO 1

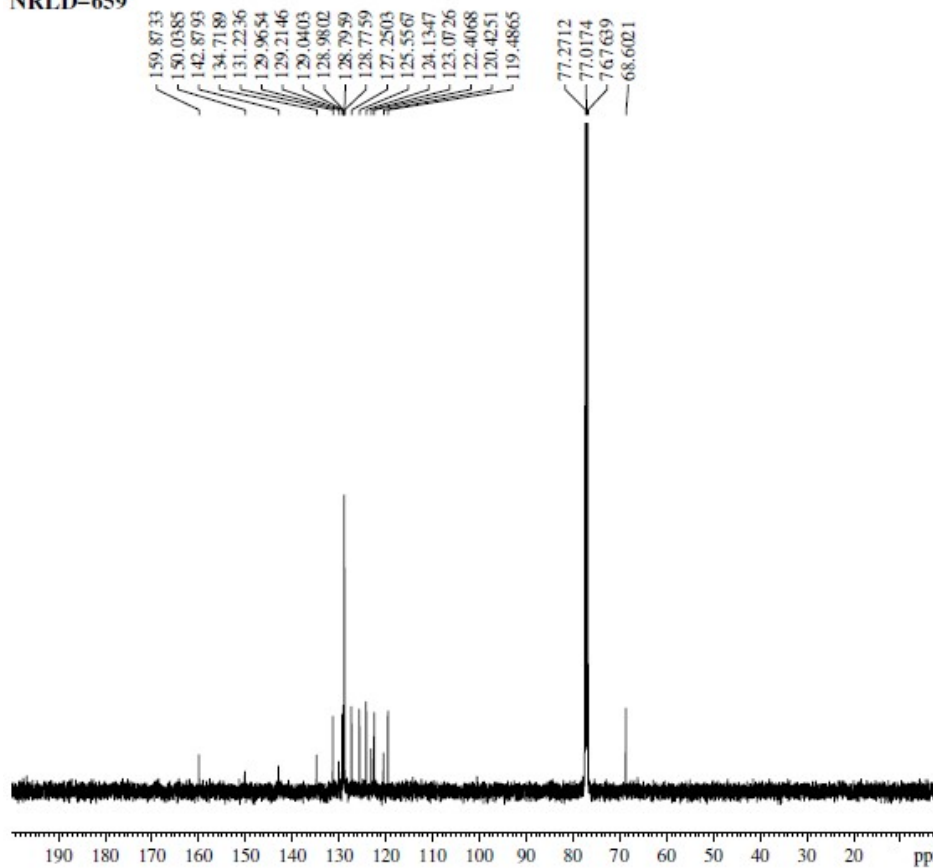
F2 - Acquisition Parameters
 Date_ 20211207
 Time 10.18
 INSTRUM spect
 PROBHD 5 mm PATX1 1H/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 10026.738 Hz
 FIDRES 0.152996 Hz
 AQ 3.2680619 sec
 RG 201.78
 DW 49.867 usec
 DE 6.50 usec
 TE 303.0 K
 D1 1.00000000 sec
 TD0 1

==== CHANNEL f1 ====
 SFO1 500.6794419 MHz
 NUC1 1H
 P1 6.45 usec
 PLW1 13.6000038 W

F2 - Processing parameters
 SI 65536
 SF 500.6763720 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

Figure S65: ¹H NMR spectrum of 3zc

NRLD-659



Current Data Parameters
 NAME 09-Dec-AN-2021
 EXPNO 600
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20211209
 Time 22.02
 INSTRUM spect
 PROBHD 5 mm PATX1 1H/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 4096
 DS 0
 SWH 29761.904 Hz
 FIDRES 0.454131 Hz
 AQ 1.1010048 sec
 RG 56.22
 DW 16.800 usec
 DE 6.50 usec
 TE 303.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

==== CHANNEL f1 ====
 SFO1 125.9077573 MHz
 NUC1 13C
 P1 9.23 usec
 PLW1 244.0000000 W

==== CHANNEL f2 ====
 SFO2 500.6783527 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 80.00 usec
 PLW2 13.6000038 W
 PLW12 0.08840500 W
 PLW13 0.05657900 W

F2 - Processing parameters
 SI 32768
 SF 125.8951680 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

Figure S66: ¹³C NMR spectrum of 3zc

NRLD-668

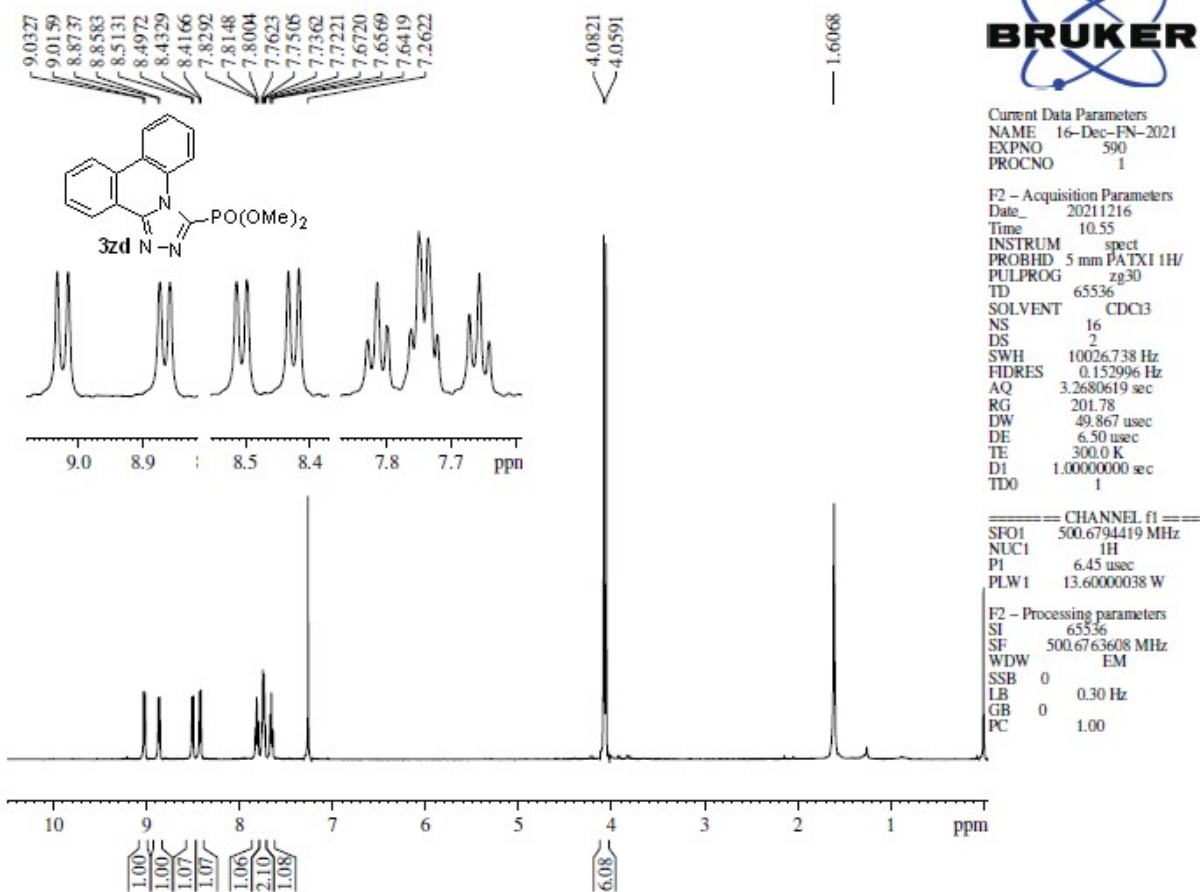


Figure S67: ¹H NMR spectrum of 3zd

NRLD-668

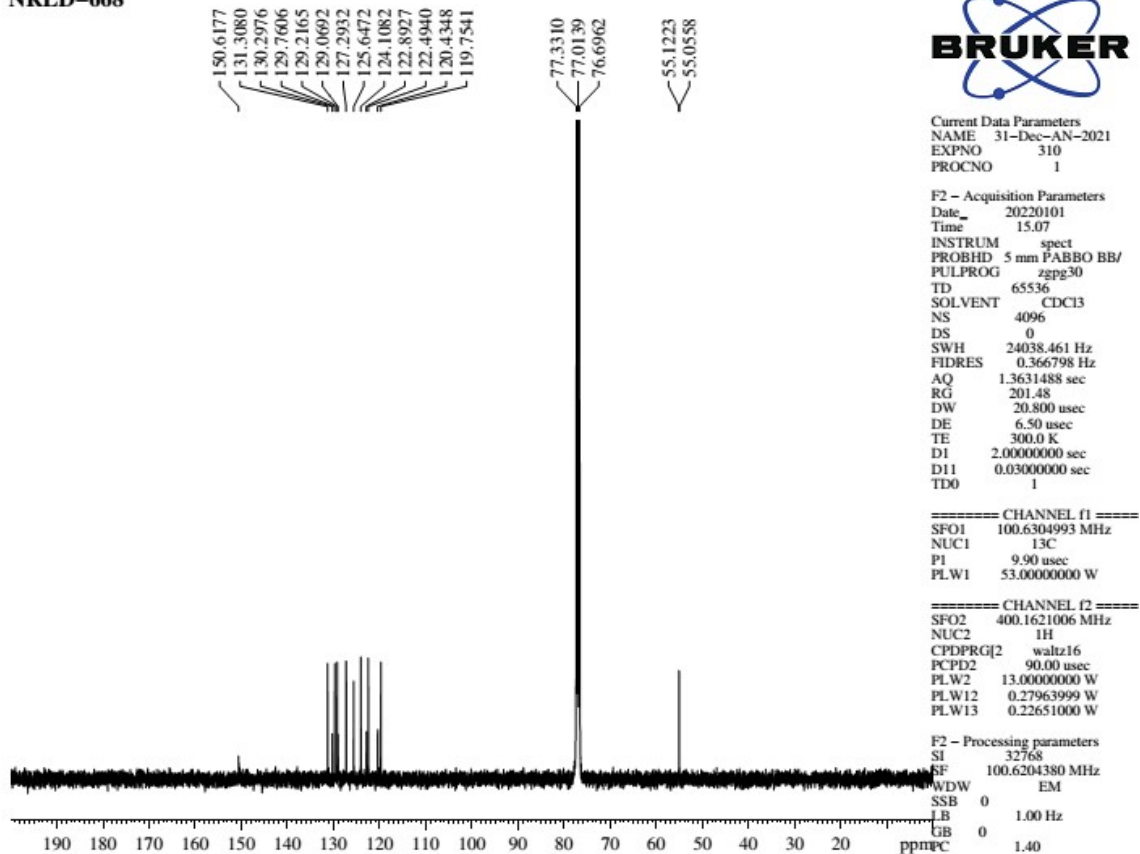


Figure S68: ¹³C NMR spectrum of 3zd

NRLD-668

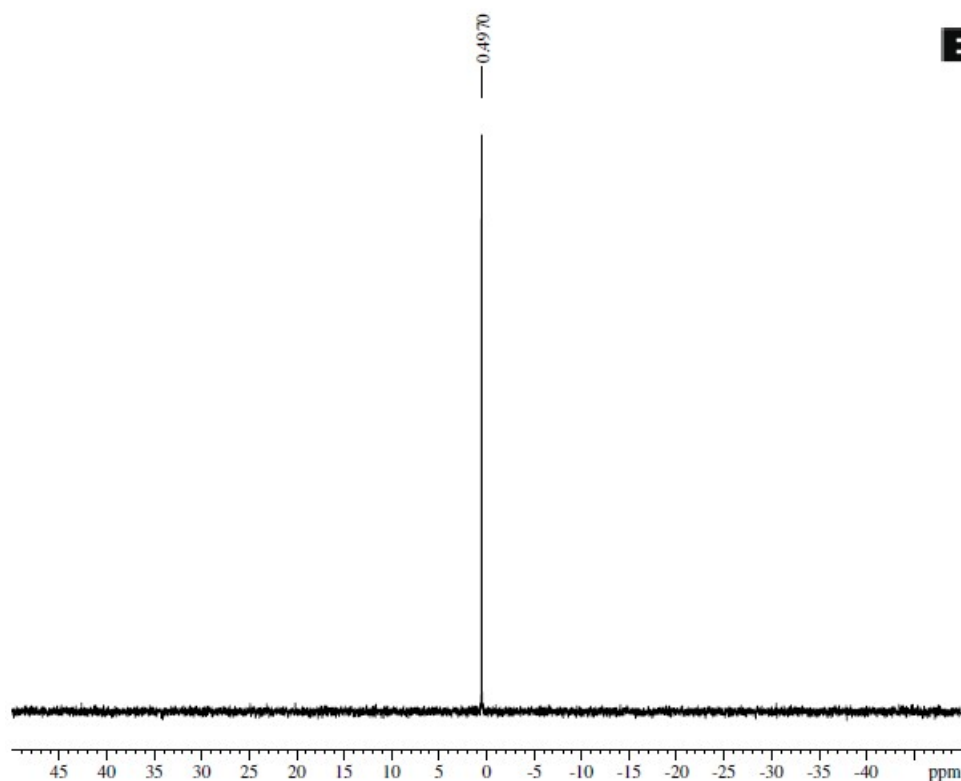


Figure S69: ³¹P NMR spectrum of 3zd



Current Data Parameters
 NAME 20-Dec-FN-2021
 EXPNO 590
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20211220
 Time 22.33
 INSTRUM spect
 PROBHD 5 mm PABBO BBV
 PULPROG zgpg30
 TD 65536
 SOLVENT DMSO
 NS 16
 DS 4
 SWH 64102.563 Hz
 FIDRES 0.978127 Hz
 AQ 0.5111808 sec
 RG 201.48
 DW 7.800 usec
 DE 6.50 usec
 TE 300.3 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

==== CHANNEL f1 =====
 SFO1 161.9798402 MHz
 NUC1 31P
 P1 15.00 usec
 PLW1 12.00000000 W

==== CHANNEL f2 =====
 SFO2 400.1621006 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 90.00 usec
 PLW2 13.00000000 W
 PLW12 0.27363999 W
 PLW13 0.22651000 W

F2 - Processing parameters
 SI 32768
 SF 161.9879400 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

NRLD-692

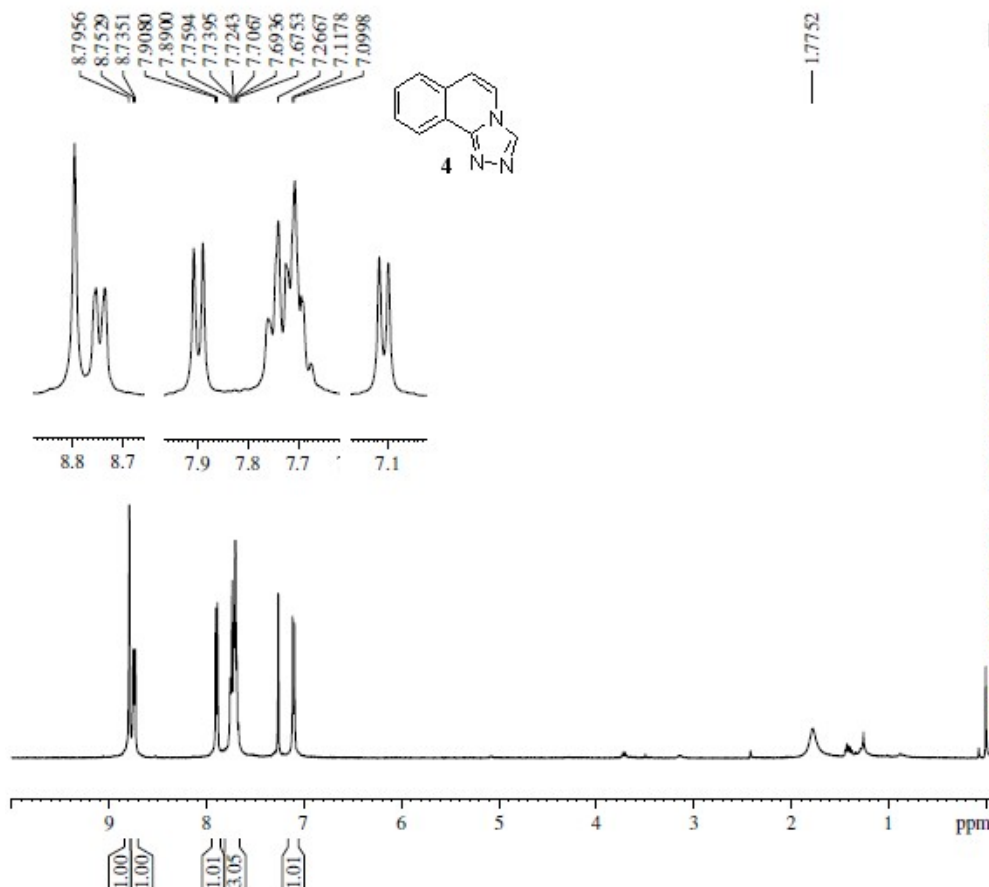


Figure S70: ¹H NMR spectrum of 4



Current Data Parameters
 NAME 28-Jan-AN-2022
 EXPNO 310
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20220128
 Time 23.06
 INSTRUM spect
 PROBHD 5 mm PABBO BBV
 PULPROG zg30
 TD 65536
 SOLVENT CDC13
 NS 8
 DS 0
 SWH 9615.385 Hz
 FIDRES 0.146719 Hz
 AQ 3.4078720 sec
 RG 159.22
 DW 52.000 usec
 DE 6.50 usec
 TE 300.0 K
 D1 1.00000000 sec
 TD0 1

==== CHANNEL f1 =====
 SFO1 400.1629712 MHz
 NUC1 1H
 P1 13.20 usec
 PLW1 13.00000000 W

F2 - Processing parameters
 SI 65536
 SF 400.1605070 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

NRLD-692

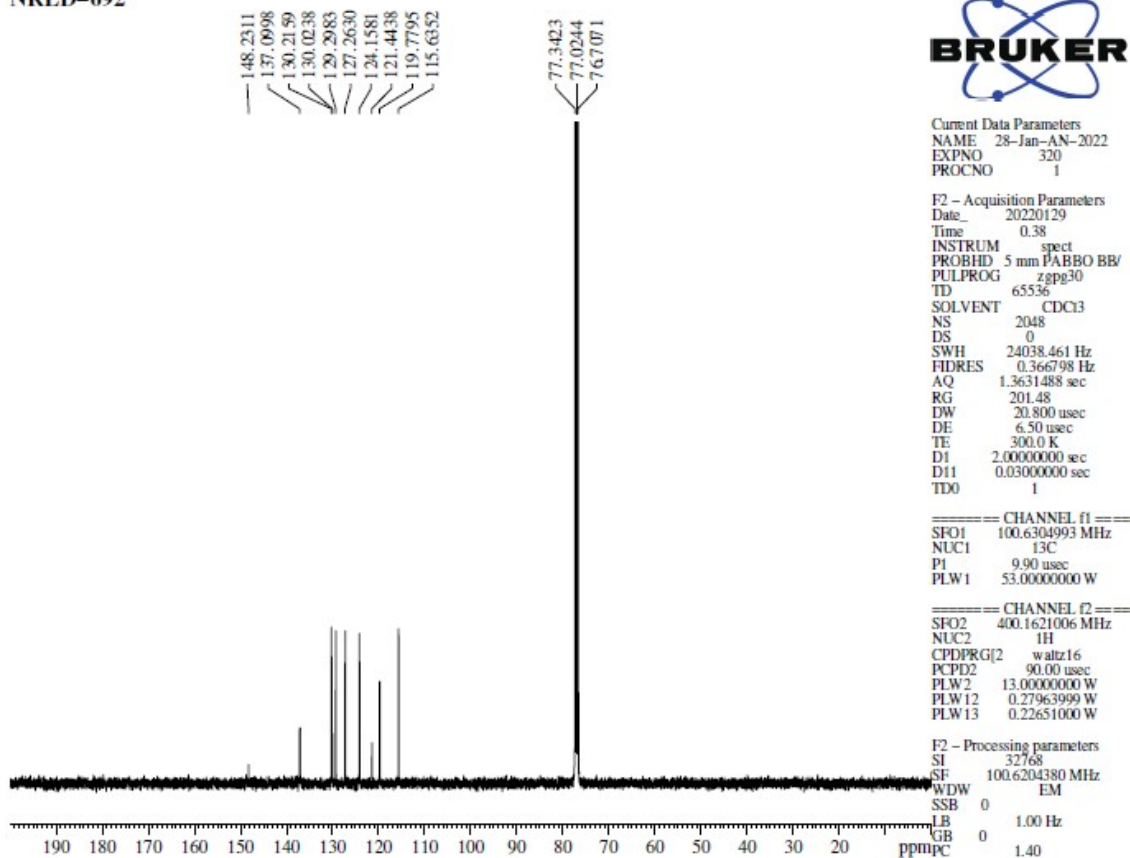


Figure S71: ¹³C NMR spectrum of 4

NRLD-693

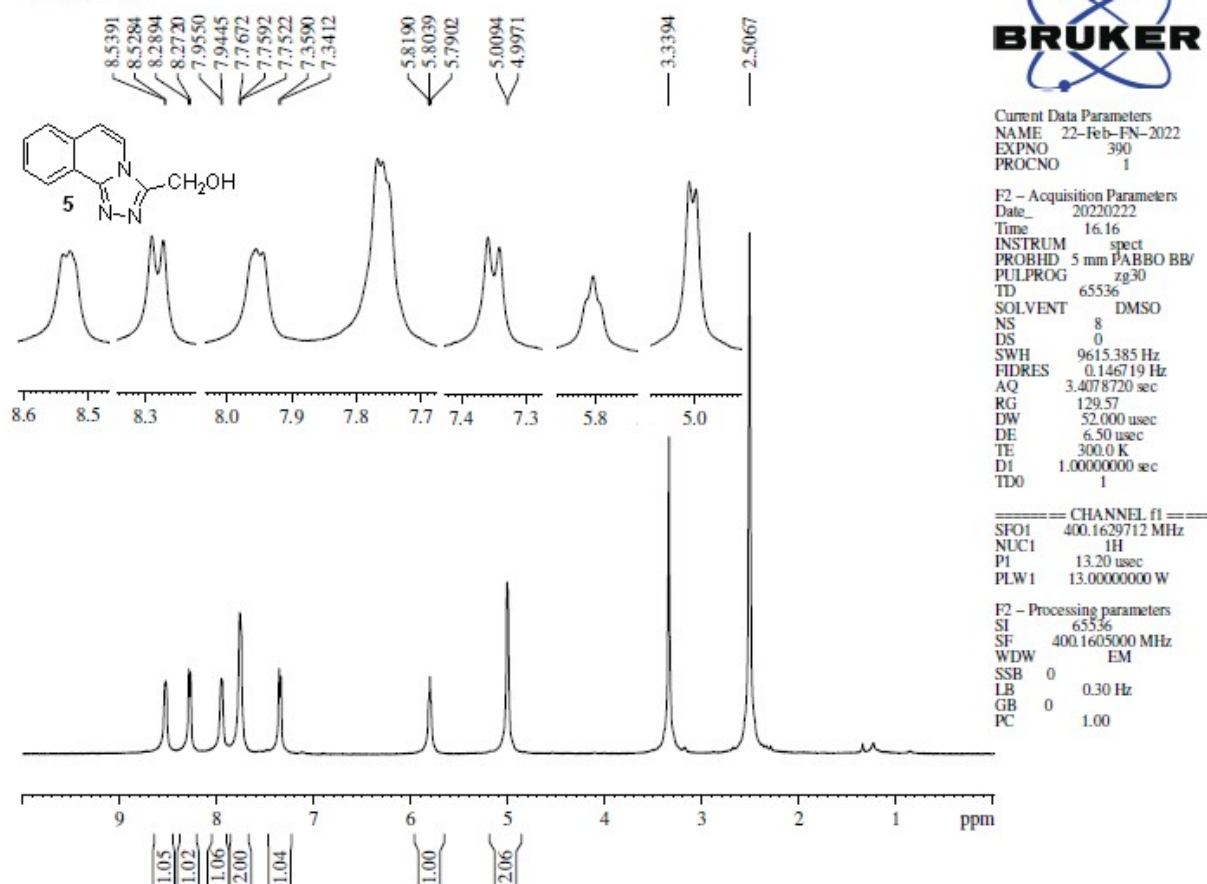


Figure S72: ¹H NMR spectrum of 5

NRLD-693

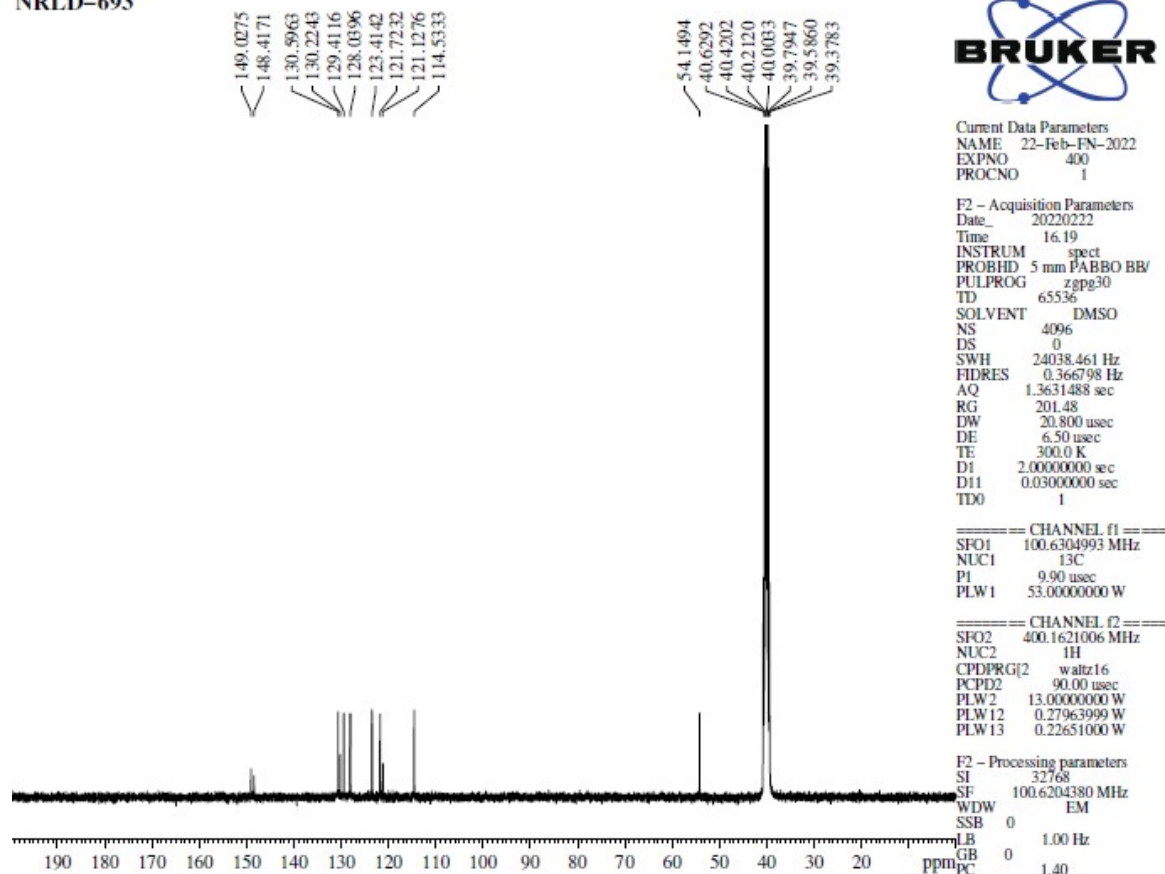


Figure S73: ¹³C NMR spectrum of 5

NRLD-689

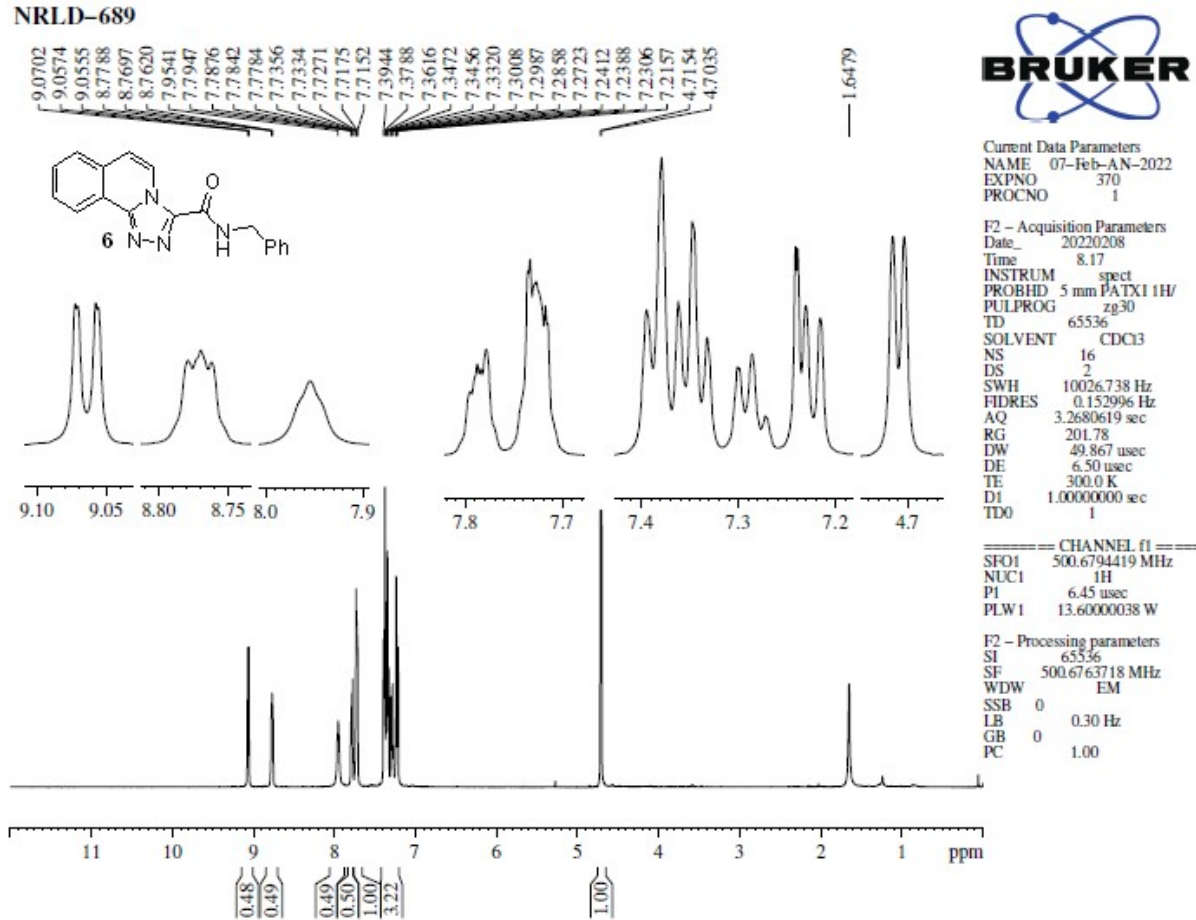


Figure S74: ¹H NMR spectrum of 6

NRLD-689

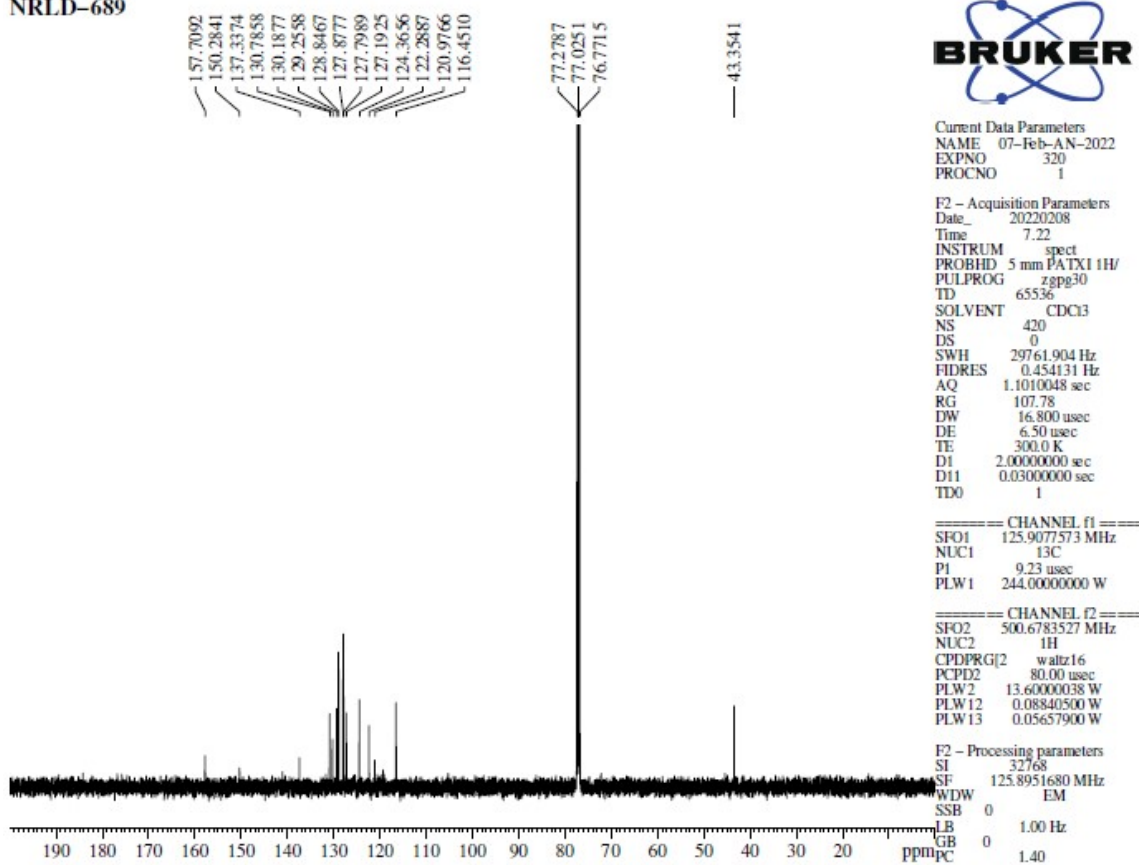


Figure S75: ¹³C NMR spectrum of 6